ELECTROMAGNETIC TECHNIQUES IN SOME PROBLEMS OF PHYSICS AND BIOLOGY

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PREFACE

This dissertation is an account of work carried out in the Department of Applied Mathematics of the Institute of Advanced Studies in the Australian National University between November 1974 and February 1978, under the supervision of Prof. Barry W. Ninham.

While I have benefited greatly from discussions with other members of the Department, especially Professor B.W. Ninham, Drs. D.Y.C. Chan and D.J. Mitchell, as well as Dr S.W. Thorne from Division of Plant Industry, CSIRO, the material presented is my own, unless specifically stated.

None of the work reported here has been submitted to any other institute of learning for any degree.

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LIST OF PUBLICATIONS

1. On a mixed value problem for linear plasma electrodynamics, *IFTR* (Institute of Fundamental Technological Research) *Reports*, Warsaw, 1971 (in Polish).
2. On an initial value problem for a nonlinear system of Vlasov-Maxwell's equations, *Bull. Acad. Polon. Sci. ser. sci tech.*, 21 (1973) 97 [157].
3. The existence and uniqueness of solutions of nonlinear plasma electrodynamics equations using kinetic approach, *IFTR Reports*, Warsaw, 1973 (in Polish).
4. A mixed value problem for a linearized set of Vlasov-Maxwell's equations, *Bull. Acad. Polon. Sci. ser. sci. tech.*, 22 (1974) 13 [161].
5. On initial value problems in linear electrodynamics of dispersive media, *IFTR Reports*, Warsaw 1976 (in Polish).
6. Energy of interaction between a monolayer and a dielectric adsorbent (with B.W. Ninham), *J. Chem. Soc. Faraday Trans. II*, 72 (1976) 1513.
7. Comment on van der Waals forces between heavy alkali atoms and gold surfaces. (with B.W. Ninham), *Phys. Letters*, 59A (November 1976) 111.
8. Effect of spatial dispersion on van der Waals interactions between molecules (with J. Mahanty and B.W. Ninham), *Solid State Communications*, 23 (1977) 381.
9. The relation of light induced slow absorbancy and scattering changes about 520 nm and structure of chloroplast thylakoids - a theoretical investigation (with S.W. Thorne), in press in *Journal of Bioenergetics and Biomembranes*.

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Last, but not least, I express gratitude to my wife, Jadwiga. I feel that without her moral support the whole endeavour would not have been worthwhile.

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MOTIVATION

During the three years of my study leading to this thesis I developed a feeling that if I had picked one particular subject I would have lost contact with the developments in other areas. I decided, therefore, to seek common properties of various disciplines, rather than pursue research in one. This desire made me look at electromagnetic theory as a tool of inquiry into a number of problems of interest to other branches of physics, and even biology. This thesis is considered as a modest contribution to the quest for unification of science.

ABSTRACT

The first chapter of the thesis was intended primarily to show the link between classical electromagnetic theory and van der Waals forces theory, and provide background for the next three chapters. In the process of writing it assumed, however, a secondary role as well, which is a critical review of existing theories of dispersion forces. A common deficiency of these theories is pointed out.

Chapters 2, 3 and 4 are all concerned with van der Waals forces acting on molecules near the surface of a macroscopic body. In Chapter 2 a formulation of the problem in terms of the scattered (or reflected) electromagnetic Green's function is given and the interaction between molecules near a dielectric and metallic halfspace is considered. It is found that in many practical applications, e.g. physical adsorption, the effect of spatial dispersion of metals can be neglected.

Chapter 3 deals with dispersion forces in adsorption problems. The correction due to the substrate to the critical temperature for two-dimensional condensation is calculated and shown to fit with experimental data. The Green's function technique for calculating adsorption energies in topographical active sites on the substrate, such as steps and pores, is developed. The chapter ends with a critical discussion of results of some measurements of van der Waals forces between alkali atoms and gold surfaces. An explanation for the apparent discrepancy between theory and experiment is given.

Van der Waals forces between moving bodies is the subject of Chapter 4. The frictional force acting on a moving neutral molecule near a dielectric and metallic halfspace is calculated. The conclusion is reached that the force is not significant in most practical situations.

The Hertz-Debye potential technique, well known in scattering theory, is used in Chapter 5 for the calculation of luminescence radiative lifetimes of molecules in solutions. The semiclassical linear oscillator model is used to describe the luminescent molecule. Contrary to popular assumptions, it is shown that the fluorescent radiative lifetime strongly depends on the properties of the solvent.

In Chapter 6 scattering theory is applied to the biological problem of the 520 nm difference absorption band of chloroplasts. It is suggested that the selective, or anomalous, dispersion of the refractive index of particles in chloroplasts is responsible for the observed phenomenon, which has remained obscure in photosynthetic research for some years.

CHAPTER 1

ELECTROMAGNETIC CHARACTER OF VAN DER WAALS FORCES

1.1 Introduction

This chapter serves the purpose of introducing a general theory and describing notation needed in other chapters. It evolved during the process of writing into a personal review of the theory of dispersion forces putting special emphasis on the link between the normal mode [1-3] approach and the fluctuation-dissipation method [4-6] of deriving dispersion free energies. These two aspects of Chapter 1 made it more detailed than a typical introduction to the subject. The question of validity of the general theory is also discussed here.

We begin with a discussion of the range of phenomena where van der Waals forces play an important role. Next we describe the ideas behind the intuitive theory of van Kampen *et al* [1], where the dispersion energy in a system is given in terms of the zero-point energy of the normal modes of electromagnetic fields supported by the system. We take up the normal mode analysis in the next section and relate the zero-point energy of a system of ideal harmonic oscillators to the density of states and the quantum-mechanical Green's function, in a rigorous manner.

In Section 3 we pursue the Green's function method, and consider a system of nonpolar neutral molecules for which we derive the dispersion energy in terms of the dipole-dipole macroscopic response function. In the last section we give a general derivation of the dispersion free energies based on the fluctuation-dissipation theorem. An expression for the dispersion free energy involving the macroscopic electrodynamic Green's function is given. This expression is equivalent

to that obtained through the normal mode approach. It does not seem, however, to be accurate when used in calculating bulk energies, except for the low density limit. It is nonetheless accurate if applied to the case of *interactions* between separate bodies.

The intersection of the fields of biology, physics and chemistry embraces phenomena which may be classified as belonging to the border region between the micro- and macro-world. It is in this region that van der Waals, or dispersion forces together with other types of interactions such as structural [7] and electrostatic [8] play an important role. Consider, for example, two colloidal particles in a solution. By changing the surface charge of the particles one can influence the electrostatic part of the interaction between them, and in particular, eliminate it completely. By increasing the distance between them the force due to the solvent structure can be eliminated as well. Yet the van der Waals force cannot be destroyed by any method; and this distinguishes it from all the other types of interactions [9].

Since van der Waals forces have this universal character, and do not depend on the charge or multipole moment of the particles involved, one cannot explain them on the grounds of classical electrodynamics itself, and one has to resort to quantum mechanics for an answer. In this way London theoretically calculated the long-range forces between neutral nonpolar molecules. An extension of this result to calculating the force between two macroscopic bodies by means of pairwise summation of London forces between the constituent molecules is, however, valid only in the low density limit, where one can neglect three- and many-body interactions. Lifshitz [4] was the first to derive rigorously an expression for the force between two macroscopic bodies. The Lifshitz theory was also the first that linked classical electrodynamics and dispersion interactions.

Nowadays there are a number of derivations for the dispersion free energies in various systems; and we refer to monographs [3,10] and reviews [6,11,12] for particulars. Here we discuss briefly one such derivation due to Van Kampen, Nijboer and Schramm [1], as it provides an elegant, though intuitive and heuristic, method for relating the dispersion interaction energies to the properties of macroscopic electromagnetic fields.

To illustrate this method we consider, after Ninham, Parsegian and Weiss [2], two semi-infinite dielectric media, separated by a vacuum gap of width ℓ. The fluctuating electromagnetic field in the gap is due to dipole moments of molecules in both media. By Planck's hypothesis [13], the energy associated with this field can be expressed as the sum of energies of the elementary oscillators-photons constituting the field. The photons are identified with Fourier components of the field, which are called modes.

We are interested in these components of the fluctuating electromagnetic field which are due to the inhomogeneity in the system, i.e. which would disappear when both media were identical and the width of the gap ℓ would equal zero. These components are called surface modes, and are obtained by solving Maxwell's equations without sources with appropriate boundary conditions at the surfaces of the dielectrics. In general one obtains a necessary condition for the existence of non zero solutions. Without specifying for the time being the actual form of this condition, we write it in the form:

$$D(\alpha,\omega) = 0 \qquad (1.1)$$

where ω is the frequency and α stands symbolically for other parameters. Eq (1.1) yields solutions ω_α which are the frequencies of electromagnetic fields supported by the system. To each frequency ω_α is assigned the

zero-point energy of a corresponding photon: $E_\alpha = \frac{1}{2}\hbar\omega_\alpha$ [13]. When the temperature in the system, T, is finite one should consider the free energy of the photon, F_α, rather than E_α [14]:

$$F_\alpha = \frac{1}{\beta} \log[2\sinh(\hbar\omega_\alpha\beta/2)] \ , \tag{1.2}$$

where $\beta = 1/kT$, k is Boltzmann's constant.

The total free energy associated with the surface modes is simply the sum of individual free energies F_α over all possible parameters α. It can be shown [2] that this sum can be expressed in a form involving the secular determinant $D(\alpha,\omega)$ of eq (1.1):

$$F = \sum_\alpha F_\alpha = \frac{1}{\beta} \sum_{n=0}^{\infty}{}' \sum_\alpha \log D(\alpha, i\xi_n) \tag{1.3}$$

where $\xi_n = 2\pi n/\hbar\beta$ and prime on the summation means that the n=0 term is multiplied by half.

In the present example the secular determinant assumes the form:

$$D(k_x,k_y;\omega) = 1 - \frac{[\varepsilon_1(\omega)-1][\varepsilon_2(\omega)-1]}{[\varepsilon_1(\omega)+1][\varepsilon_2(\omega)+1]} \exp(-2\sqrt{k_x^2+k_y^2}\,\ell) \tag{1.4}$$

where $\underline{k} = (k_x,k_y)$ is the two-dimensional wave vector parallel to the surfaces of the dielectrics and $\varepsilon_1(\omega)$, $\varepsilon_2(\omega)$ are their permittivities. Eq (1.4) has been derived under assumption that the distance ℓ is much smaller than a typical wavelength of ultraviolet absorption, $\lambda_0 = 2\pi/\omega_0$ (≈ 500 Å). In such circumstances one can consider the nonretarded approximation, i.e. let $c \to \infty$ in Maxwell's equations*.

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* The reason for this is that $\varepsilon_i(\omega)$ for $\omega > \omega_0$ quickly converges to 1; thus only the components of the field with $\omega < \omega_0$ contribute significantly to the free energy F. For these frequencies, however, the phase difference over a distance $\ell \ll \lambda_0$ is negligible, hence one can use the quasistatic limit of Maxwell's equations.

Substituting (1.4) into (1.3) and taking the limit $T \to 0$ we obtain the expression for the free energy per unit area:

$$F/(\text{unit area}) = \frac{1}{\ell^2} \frac{\hbar}{(2\pi)^2} \int_0^\infty d\xi \int_0^\infty x dx \log(1-\Delta_{10}\Delta_{20}e^{-2x}) \qquad (1.5)$$

where $\Delta_{j0} = (\varepsilon_j(i\xi)-1)/(\varepsilon_j(i\xi)+1)$, $j = 1,2$.
The free energy per unit area varies, therefore, with the distance as $1/\ell^2$; hence the force between the two dielectric halfspaces goes like $1/\ell^3$.

Lifshitz [4] obtained the same result with the aid of a more complicated formalism. Now the question to be asked is whether eq (1.3) can be used in other situations especially when the concept of the surface modes loses its sense [6] as is so in the case of absorbing media. We shall examine this problem in subsequent sections.

1.2 The quantum mechanical energy of a system of ideal harmonic oscillators - normal mode analysis.

Harmonic oscillators usually provide a good example of a model which is close to real systems and yet amenable to a simple mathematical treatment. We take up this model to discuss the relation between the quantum-mechanical energy of the system and the Green's function which depends on its dynamical characteristics.

Consider N coupled harmonic oscillators whose equations of motion are:

$$\ddot{\underline{x}} = -\underline{\underline{A}}\,\underline{x} \qquad (1.6)$$

where $\underline{\underline{A}}$ is a symmetric $N \times N$ matrix for which the following condition is satisfied:

$$\underline{x} \cdot \underline{\underline{A}}\,\underline{x} > 0 \quad \text{if} \quad |\underline{x}| > 0. \tag{1.7}$$

It follows from the elementary theory of linear ordinary differential equations (e.g. Pontryagin [15]) that each solution of eq (1.6) can be considered as a linear superposition of normal modes, i.e. oscillations with a single frequency. By the quantum mechanical prescription we assign to each mode a zero-point energy $\hbar\omega/2$, where ω is the frequency of the mode. This assumption means in practice that a real system represented by the coupled oscillators remains at a very low temperature. Now the energy of the system is the sum of energies of all modes:

$$E = \sum_{\text{all modes}} \hbar\omega/2 = \frac{\hbar}{2} \int_0^\infty \omega\rho(\omega)\,d\omega \quad . \tag{1.8}$$

where we have introduced $\rho(\omega)$, the density of modes:

$$\rho(\omega) = \sum_{\ell=1}^{N} \delta(\omega-\omega_\ell) \tag{1.9}$$

and $\delta(\omega-\omega_\ell)$ is the Dirac delta function. We shall now find the relationship between the density of states and the dynamic properties of the system incorporated in the matrix $\underline{\underline{A}}$.

Let us denote the normalized eigenvectors of $\underline{\underline{A}}$ by $\underline{\zeta}^\ell$, $\ell = 1,2,\ldots,N$, and the corresponding eigenvalues by ω_ℓ^2, that is we have:

$$\text{a)}\ \ \underline{\underline{A}}\,\underline{\zeta}^\ell = \omega_\ell^2\,\underline{\zeta}^\ell\ , \qquad \text{b)}\ \ \underline{\zeta}^\ell \cdot \underline{\zeta}^j = \delta_j^\ell \equiv \begin{cases} 1 & \text{when } \ell = j \\ 0 & \text{when } \ell \neq j \end{cases} \tag{1.10}$$

For simplicity let $\omega_\ell \neq \omega_m$, if $\ell \neq m$, though this is not essential. Suppose now that at time $t=0$ an impulsive force is applied to the j-th particle and that for $t < 0$ the system was at rest. The response of the system to this force, $\underline{g}_j(t) = (g_j^1(t),\ldots,g_j^N(t))$, is called the

vector Green's function and satisfies the equation

$$\ddot{\underline{g}}_j + \underline{\underline{A}}\,\underline{g}_j = -\delta(t)\underline{e}_j \tag{1.11}$$

where $\underline{e}_j$ is the j-th vector of the orthonormal basis in the N-dimensional space. The vector Green's function can be considered as the j-th column of the N×N matrix $\underline{\underline{G}} = \left\{g_j^k(t)\right\}$, where, say, the element $g_j^k(t)$ describes the response of the k-th particle to a unit impulse applied to the j-th particle. Multiplying eq (1.11) by $\underline{\zeta}^\ell$ and denoting $b_j^\ell \equiv \underline{g}_j \cdot \underline{\zeta}_\ell$ we obtain:

$$\ddot{b}_j^\ell + \omega_\ell^2 b_j^\ell = -(\underline{e}_j \cdot \underline{\zeta}_\ell)\delta(t) \ . \tag{1.12}$$

Since the system before $t=0$ was at rest, the solution to eq (1.12) must have the form:

$$b_j^\ell(t) = -\theta(t)(\underline{e}_j \cdot \underline{\zeta}_\ell)\frac{\sin\omega_\ell t}{\omega_\ell} \tag{1.13}$$

where $\theta(t) = \begin{cases} 0 \ , & \text{for } t < 0 \\ 1 \ , & \text{for } t > 0 \end{cases}$.

In order to find $g_j^k(t)$ we need to multiply $\underline{g}_j(t)$ by $\underline{e}_k$, and because $\underline{g}_j(t)$ is represented as

$$\underline{g}_j(t) = \sum_{\ell=1}^{N} b_j^\ell(t)\,\underline{\zeta}_\ell \tag{1.14}$$

we obtain from (1.14) and (1.12):

$$g_j^k(t) = \underline{e}_k \cdot \underline{g}_j(t) = -\theta(t) \sum_{\ell=1}^{N} (\underline{e}_k \cdot \underline{\zeta}_\ell)(\underline{e}_j \cdot \underline{\zeta}_\ell)\frac{\sin\omega_\ell t}{\omega_\ell} \ . \tag{1.15}$$

We shall now find the Fourier transform of the Green's function:

$$\tilde{g}_j^k(\omega) = \int_{-\infty}^{+\infty} dt\ e^{i\omega t} g_j^k(t) \ . \tag{1.16}$$

Bearing in mind the Fourier representation of the $\theta(t)$

$$\int_{-\infty}^{+\infty} \theta(t) e^{i\omega t} dt = P \frac{i}{\omega} + \pi\delta(\omega) \tag{1.17}$$

where P denotes the principal value, from (1.15) we obtain

$$\tilde{g}_j^k(\omega) = \sum_{\ell=1}^{N} (\underline{e}_k \cdot \underline{\zeta}_\ell)(\underline{e}_j \cdot \underline{\zeta}_\ell) \left[P \frac{1}{\omega^2 - \omega_\ell^2} + \right.$$

$$\left. - \frac{\pi i}{2\omega_\ell} (\delta(\omega-\omega_\ell) + \delta(\omega+\omega_\ell)) \right] . \tag{1.18}$$

As we are interested only in the case $\omega \geqslant 0$, we have

$$\text{Im } \tilde{g}_j^k(\omega) = - \frac{\pi}{2\omega} \sum_{\ell=1}^{N} \delta(\omega-\omega_\ell)(\underline{e}_k \cdot \underline{\zeta}_\ell)(\underline{e}_j \cdot \underline{\zeta}_\ell) . \tag{1.19}$$

We can see now how the density of modes $\rho(\omega)$ is related to the spectral form of the Green's function. From eqs (1.19) and (1.9) we obtain

$$\rho(\omega) = - \frac{2\omega}{\pi} \text{Im} \sum_{k=j} \{\tilde{g}_j^k(\omega)\} = - \frac{2\omega}{\pi} \text{ImTr } \underline{\underline{\tilde{G}}}(\omega) \tag{1.20}$$

where we have made use of the fact that the bases $\{\underline{\zeta}_\ell\}$ and $\{\underline{e}_\ell\}$ are orthonormal. Substituting (1.20) into (1.8) yields

$$E = - \frac{\hbar}{\pi} \int_0^\infty \omega^2 \text{Im Tr } \underline{\underline{\tilde{G}}}(\omega) \, d\omega . \tag{1.21}$$

Eq (1.21) can also be written in an alternative form which will be useful when comparing this idealized semiclassical model with the quantum mechanical one. Multiplying eq (1.19) by the element A_{kj} of the matrix $\underline{\underline{A}}$ and performing the summation over all k and j we obtain

$$\mathrm{Im} \sum_{k,j=1}^{N} A_{kj} \tilde{g}_j^k(\omega) = -\frac{\pi}{2} \sum_{\ell=1}^{N} \frac{1}{\omega_\ell} \delta(\omega_\ell - \omega)(\underline{\zeta}_\ell \cdot \underline{\underline{A}}\, \underline{\zeta}_\ell) =$$

$$= -\frac{\pi}{2} \sum_{\ell=1}^{N} \omega_\ell \delta(\omega - \omega_\ell) = -\frac{\pi}{2} \rho(\omega) \quad . \tag{1.22}$$

From the last equation and (1.8) we obtain an alternative form for the energy which is

$$E = -\frac{\hbar}{\pi} \int_0^\infty \mathrm{Im}\, \mathrm{Tr}\, \underline{\underline{A}}\, \underline{\underline{\tilde{G}}}(\omega) d\omega \quad . \tag{1.23}$$

In sum we may say that the quantum mechanical vibrational energy of a system of harmonic oscillators, being the sum of the energies of all modes allowed in the system, can be represented in terms of the spectral form of the dynamic response of the system to unit impulses, or, in other words, in terms of the response to sinusoidal forces.

1.3 Dispersion energy in a system of interacting polarizable molecules - the zero-temperature approximation.

We turn to a more rigorous approach to the theory of van der Waals forces with an example of a discrete system of nonpolar and neutral molecules. Starting from the microscopic description of the system by its Hamiltonian we shall obtain the expression for the dispersion energy due to fluctuating dipole moments of the constituent molecules. The final result is identical with one obtained by the normal mode analysis for this case [10].

The quantum description of our system requires the knowledge of the total Hamiltonian, H, in which all types of interactions involved have their respective terms. To avoid complications connected with the interactions between excited molecules, we shall assume that the system is in its lowest energy state which is described by the wavefunction

$|\psi_0>$. This corresponds to the assumption that the temperature T is so small that the thermal energy $kT \ll E_1 - E_0$, where E_1 and E_0 are the first and the ground energy levels in the system. When this is satisfied then the most likely state of the system is the ground state.

In the Hamiltonian of the system we encounter terms corresponding to internal structures of the molecules, and terms reflecting their mutual interaction. We select these which are due to the dipole-dipole interactions between the molecules and group them together in the Hamiltonian H_1. In other words, the total Hamiltonian H is split into two terms: H_0 and H_1, where H_1 contains only the dipole-dipole interactions between the molecules.*

The problem we tackle is the following: find that part of the ground state energy due to the interactions described by H_1. This amounts to calculating the difference between the ground state energy in the system described by the full Hamiltonian $H = H_0 + H_1$, and the fictitious system for which the Hamiltonian is H_0. It can be shown that this difference can be calculated by evaluating the following integral [5]:

$$\Delta E_0 = \int_0^1 \frac{\partial}{\partial\lambda} <\psi_0(\lambda)|H(\lambda)|\psi_0(\lambda)> d\lambda \qquad (1.24)$$

where the Hamiltonian $H(\lambda)$ is defined by

$$H(\lambda) = H_0 + \lambda H_1 \qquad (1.25)$$

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* We tacitly assume that the multipole contribution to the interaction between the molecules is not significant, and omit the corresponding term completely - thus H_0 describes only the internal structure of the molecules. Higher order contributions to dispersion interactions have been considered by Richardson [16].

and $|\psi_0(\lambda)>$ is the ground state corresponding to $H(\lambda)$. Note that $H(1) = H \equiv H_0 + H_1$ and $H(0) = H_0$.

Let N be the number of the molecules in our system; $\underline{R}_1,\ldots,\underline{R}_N$ their positions, and $\underline{P}_1,\ldots,\underline{P}_N$ the operators of their dipole moments. We shall assume throughout this section that the Latin indices i,j,k, etc. refer to particular molecules and the Greek indices μ,ν,ρ, etc. refer to Cartesian components of vectors and tensors. In view of this convention we shall write the Hamiltonian H_1 as

$$H^1 = \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\mu,\nu=1}^{3} A_{ij}^{\mu\nu} P_i^{\mu} P_j^{\nu} \tag{1.26}$$

where the coefficients $A_{ij}^{\mu\nu}$ are given by

$$A_{ij}^{\mu\nu} = \left\{ \nabla_{\underline{R}_i} \nabla_{\underline{R}_j} \frac{1}{|\underline{R}_i - \underline{R}_j|} \right\}_{\mu\nu} \tag{1.27}$$

that is, for fixed i and j, they are the components of the dipole-electric field Green's function dyadic in the free space.

From eqs (1.26), (1.25) and (1.24) we can write the energy in the form

$$\Delta E_0 = \frac{1}{2} \sum_{i,j} \sum_{\mu,\nu} \int_0^1 \frac{d\lambda}{\lambda} A_{ij}^{\mu\nu} <\psi_0(\lambda)|\lambda P_i^{\mu} P_j^{\nu}|\psi_0(\lambda)> . \tag{1.28}$$

Thus, in order to calculate the dispersion energy we need to find the expectation values of $\lambda P_i^{\mu} P_j^{\nu}$ in the ground state of fictitious systems described by the Hamiltonians (1.25) for $0 \leqslant \lambda \leqslant 1$. This can be achieved by expressing these values in terms of the spectral form $\underline{\underline{\tilde{G}}}(\omega,\lambda)$ of the quantum Green's function $\underline{\underline{G}}(t,\lambda) = \{g_{ij}^{\mu\nu}(t,\lambda)\}$. In what follows we suppress, for convenience, the dependence on the parameter λ.

The quantum Green's function is an important concept which helps to bridge the microscopic and macroscopic properties of the matter. We set aside more detailed discussion of general properties of the Green's functions until the next section. Here we merely define the Green's function $g_{ij}^{\mu\nu}(t)$ as the average value of the μ-th component of the dipole moment induced on the i-th molecule at time $t > 0$ by an impulsive force applied at $t = 0$ to the j-th molecule. This force is interpreted as a unit amplitude electric field whose only one Cartesian component, ν, is different from zero. Therefore, the input of the energy to the system is described by the addition of the following term to the Hamiltonian:

$$H^1 = -P_j^{\nu}\delta(t) \quad . \tag{1.29}$$

By definition then, the Green's function $g_{ij}^{\mu\nu}(t)$ is determined as

$$g_{ij}^{\mu\nu}(t) \equiv \langle \psi(t) | P_i^{\mu} | \psi(t) \rangle , \qquad t > 0 \tag{1.30}$$

where the state $|\psi(t)\rangle$ is the state of the system after the perturbation at $t=0$.

The wave function $|\psi(t)\rangle$ obeys the Schrödinger equation with the Hamiltonian $H - P_j^{\nu}\delta(t)$ and satisfies the initial condition: $|\psi(t)\rangle = e^{-iE_0 t/\hbar}|\psi_0\rangle$ for $t < 0$. We shall employ first order perturbation theory to find an approximate solution of the Schrödinger equation. By the standard prescription we solve the equation:

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = H|\psi\rangle - P_j^{\nu}\delta(t)|\psi_0\rangle \tag{1.31}$$

which follows from the Schrödinger equation when we neglect terms of

the second and higher orders with respect to the difference $\psi(t) - \psi_0 \exp(-iE_0 t/\hbar)$. It is easy to prove that the function which satisfies (1.31) and the initial condition is:

$$|\psi(t)> = e^{-iE_0 t/\hbar}|\psi_0> + \\ - \frac{\theta(t)}{i\hbar} \sum_{n=0}^{\infty} (P_j^{\nu})_{n0} e^{-iE_n t/\hbar}|\psi_n> \tag{1.32}$$

where $(P_j^{\nu})_{n0} = <\psi_n|P_j^{\nu}|\psi_0>$; $\{|\psi_n>\}$ is the complete set of states and $\{E_n\}$ the energies for the unperturbed Hamiltonian H. Substituting eq (1.32) into (1.30) and retaining only leading terms we obtain

$$g_{ij}^{\mu\nu}(t) = - \frac{\theta(t)}{i\hbar} \sum_n \left\{ (P_i^{\mu})_{0n}(P_j^{\nu})_{n0} e^{-i\omega_{n0}t} + \right. \\ \left. - (P_j^{\nu})_{0n}(P_i^{\mu})_{n0} e^{i\omega_{n0}t} \right\} \tag{1.33}$$

where $\omega_{n0} = (E_n - E_0)/\hbar$. Applying now the Fourier transform to eq (1.33) we find the spectral form of the Green's function as

$$\tilde{g}_{ij}^{\mu\nu}(\omega) = - \frac{1}{\hbar} \sum_n \left\{ \left[\frac{(P_j^{\nu})_{0n}(P_i^{\mu})_{n0}}{\omega - \omega_{n0}} - \frac{(P_i^{\mu})_{0n}(P_j^{\nu})_{n0}}{\omega + \omega_{n0}} \right] \right. \\ \left. + \pi i \left[(P_i^{\mu})_{0n}(P_j^{\nu})_{n0} \delta(\omega - \omega_{n0}) - (P_j^{\nu})_{0n}(P_i^{\mu})_{n0} \delta(\omega + \omega_{n0}) \right] \right\} . \tag{1.34}$$

Taking the complex conjugate of the above expression and interchanging the indices $i \leftrightarrow j$, $\mu \leftrightarrow \nu$ we see that the first term in the square brackets on the r.h.s. remains unchanged whilst the other changes the sign. If in addition we limit ourselves to $\omega \geqslant 0$ we obtain

$$\sum_n (P_i^{\mu})_{0n}(P_j^{\nu})_{n0} \delta(\omega - \omega_{n0}) = - \frac{i\hbar}{2\pi} \left[\tilde{g}_{ji}^{\nu\mu}(\omega) - \tilde{g}_{ij}^{*\mu\nu}(\omega) \right] \tag{1.35}$$

where (*) denotes the complex conjugate. Because the set of states $\{|\psi_n>\}$ is complete, we can express the expectation values of $P_i^\mu P_j^\nu$ as

$$<\psi_0|P_i^\mu P_j^\nu|\psi_0> \equiv <P_i^\mu P_j^\nu> = \sum_n <\psi_0|P_i^\mu|\psi_n><\psi_n|P_j^\nu|\psi_0> \qquad (1.36)$$

On the other hand, the r.h.s. of the above equation can be obtained from (1.35) by integration with respect to ω in the limits 0 to ∞. This yields

$$<P_i^\mu P_j^\nu> = -\frac{i\hbar}{2\pi}\int_0^\infty [\,\tilde{g}_{ji}^{\nu\mu}(\omega) - \tilde{g}_{ij}^{*\mu\nu}(\omega)\,]\,d\omega \quad . \qquad (1.37)$$

Eq (1.37) is the desired relation between the expectation value of $P_i^\mu P_j^\nu$ and the spectral form of the Green's function. We can now reintroduce the parameter λ and substitute (1.37) into (1.28):

$$\Delta E_0 = \frac{\hbar}{2\pi}\sum_{i,j=1}^{N}\sum_{\mu,\nu=1}^{3} A_{ij}^{\mu\nu}\int_0^1 \frac{d\lambda}{\lambda}\int_0^\infty d\omega\, \mathrm{Im}\,\tilde{g}_{ij}^{\mu\nu}(\omega,\lambda) \quad . \qquad (1.38)$$

In the derivation of (1.38) we have used the symmetry of the coefficients $A_{ij}^{\mu\nu}$ with respect to the interchange of the indices $\mu \leftrightarrow \nu$ and $i \leftrightarrow j$. Eq (1.38) is the quantum analogue of eq (1.23) from the previous section.

One more step remains to be done; this is the interpretation of the quantum Green's functions $\tilde{g}_{ij}^{\mu\nu}(\omega)$ in terms of the classical dipole-dipole Green's dyadics, and the integration over λ of the r.h.s. of eq (1.38). To this end we note that if the i-th molecule is placed in an external oscillating field $\underline{E}_i(\omega)e^{-i\omega t}$, then the average dipole moment developed in the molecule is related to the field through the equation involving the polarizability tensor of the molecule $-\{\alpha_i^{\mu\nu}(\omega)\}$ [10]:

$$\langle p_i^{\mu} \rangle_{\omega} = \sum_{\nu=1}^{3} \alpha_i^{\mu\nu}(\omega) E_i^{\nu}(\omega) \quad , \tag{1.39}$$

where we have omitted the time factor $\exp(-i\omega t)$. On the other hand, if the electric field is due to a unit oscillating dipole at the position j ; $\underline{p}_j(t) = \underline{n}^{\nu}\exp(-i\omega t)$, where $\underline{n}^{\nu}$ is the unit vector in the ν direction, then by virtue of the definition of the Green's function (1.30), where we go over to the spectral form, we obtain:

$$\langle p_i^{\mu} \rangle_{\omega} = \tilde{g}_{ij}^{\mu\nu}(\omega) \ . \tag{1.40}$$

Comparing eqs (1.40) and (1.39) yields the desired relationship between the quantum Green's functions and the macroscopic electric field in the system due to a unit oscillating dipole.

We shall set up a system of algebraic equations for $g_{ij}^{\mu\nu}(\omega)$. With the external dipole moment $\underline{p}_j(t) = \underline{n}^{\nu}\exp(-i\omega t)$, the average moment induced in each molecule can be written as (we again omit the time factor):

$$\langle p_i^{\mu} \rangle_{\omega} = \sum_{\rho=1}^{3} \alpha_i^{\mu\rho}(\omega) \left[\delta_{ij}^{\rho\nu} - \sum_{k=1}^{N} \sum_{\sigma=1}^{3} A_{ik}^{\rho\sigma} \langle p_k^{\sigma} \rangle_{\omega} \right] \tag{1.41}$$

because the coefficients $A_{ik}^{\rho\sigma}$ are the elements of the Green's dyadic function for free space (cf. eq (1.27)). Substituting eq (1.40) into (1.41) yields the system of $3N \times 3N$ equations for the unknown functions $\tilde{g}_{ij}^{\mu\nu}(\omega)$:

$$\tilde{g}_{ij}^{\mu\nu}(\omega) = \sum_{\rho=1}^{3} \alpha_i^{\mu\rho}(\omega) \left[\delta_{ij}^{\rho\nu} - \sum_{k=1}^{N} \sum_{\sigma=1}^{3} A_{ik}^{\rho\sigma} \tilde{g}_{kj}^{\sigma\nu}(\omega) \right] \tag{1.42}$$

$i,j = 1,2,\ldots,N$ and $\mu,\nu = 1,2,3$.

Let us rewrite the system of equations (1.42) in matrix notation:

$$\underline{\underline{\tilde{G}}}(\omega) = \underline{\underline{\alpha}}(I - \underline{\underline{A}}\,\underline{\underline{\tilde{G}}}(\omega)) \tag{1.43}$$

where $\underline{\underline{A}} = \{A_{ij}^{\mu\nu}\}$ and $\underline{\underline{\alpha}} = \{\alpha_i^{\mu\nu}\delta_{ij}\}$.

The coupling constant λ can now be introduced in an unambiguous manner if we note that the dependence of the interaction Hamiltonian $H_1(\lambda)$ on λ can be formally hidden if we let each dipole moment operator $\underline{P}_i$ become $\underline{P}_i' = \lambda^{\frac{1}{2}}\underline{P}_i$. Since the dipole moment operator is proportional to the electron charge e, the same is achieved if we let $e' = \lambda^{\frac{1}{2}}e$, and perform all the operations using the modified electron charge. In particular, since the polarizability α is proportional to e^2, upon reintroduction of the parameter λ it becomes $\lambda\alpha$. Therefore the λ-dependence of the Green's function $\underline{\underline{G}}(\omega)$ is induced by letting in eq (1.43) $\alpha \to \lambda\alpha$. The solution to eq (1.43), where α becomes $\lambda\alpha$, can be written formally as:

$$\underline{\underline{\tilde{G}}}(\omega,\lambda) = \lambda(\underline{\underline{I}} + \lambda\underline{\underline{\alpha}}(\omega)\underline{\underline{A}})^{-1}\underline{\underline{\alpha}}(\omega) \ . \tag{1.44}$$

Multiplying from the right both sides of eq (1.44) by $\underline{\underline{A}}$ and then taking the trace of the product we obtain:

$$\mathrm{Tr}\{\underline{\underline{\tilde{G}}}(\omega,\lambda)\underline{\underline{A}}\} = \lambda\mathrm{Tr}\left\{\frac{\partial}{\partial\lambda}\log(\underline{\underline{I}} + \lambda\underline{\underline{\alpha}}\,\underline{\underline{A}})\right\} \tag{1.45}$$

where we have used the algebraic identity:

$$\frac{\partial}{\partial\lambda}\log(\underline{\underline{I}} + \lambda\underline{\underline{B}}) = (\underline{\underline{I}} + \lambda\underline{\underline{B}})^{-1}\underline{\underline{B}} \ . \tag{1.46}$$

Substituting eq (1.45) into (1.38) and using the identity

$$\mathrm{Tr}\log \underline{\underline{B}} = \log\det \underline{\underline{B}} \tag{1.47}$$

we obtain finally the following form for the dispersion energy:

$$\Delta E_0 = \frac{\hbar}{2\pi}\int_0^\infty d\omega\, \mathrm{Im}\log\det\left(\underline{\underline{I}} + \underline{\underline{\alpha}}(\omega)\underline{\underline{A}}\right) . \tag{1.48}$$

We shall now link the above expression to that obtained for the same system through the method described in the Introduction to this chapter [10]:

$$\Delta E_0 = \frac{\hbar}{2\pi}\int_0^\infty d\xi\, \log\det\left(\underline{\underline{I}} + \underline{\underline{\alpha}}(i\xi)\underline{\underline{A}}\right) . \tag{1.49}$$

The equivalence of equations (1.48) and (1.49) follows from the following identity:

$$f(i\xi) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{\omega f(\omega)}{\omega^2+\xi^2}\, d\omega \quad , \qquad \xi > 0 \tag{1.50}$$

valid for functions analytic in the upper-half of the complex ω-plane and vanishing sufficiently quickly as $|\omega| \to \infty$. If in addition the function $f(\omega)$ obeys the following symmetry properties:

$$\text{a)}\ \ \mathrm{Re}\, f(-\omega) = \mathrm{Re}\, f(\omega), \qquad \text{b)}\ \ \mathrm{Im}\, f(-\omega) = -\,\mathrm{Im}\, f(\omega) \tag{1.51}$$

as do the functions $\tilde{g}_{ij}^{\mu\nu}(\omega,\lambda)$ because their inverse Fourier transforms must be real quantities, then by integrating eq (1.50) with respect to ξ and using the symmetry properties (1.51) we obtain:

$$\int_0^\infty f(i\xi)d\xi = \int_0^\infty \mathrm{Im} f(\omega)d\omega \ . \tag{1.52}$$

Applying this identity in eq (1.38) and carrying through all the subsequent

operations without a change, we arrive at eq (1.49) instead of (1.48).

In concluding this section we summarize the main points: we have obtained through a first principle quantum mechanical approach the expression for the dispersion energy in a system of nonpolar neutral molecules, and this expression is the same as the one obtained by more intuitive arguments discussed in Sections 1 and 2.

1.4 Electromagnetic fluctuations and dispersion forces

1.4.1 Principles

In this final section we present the most general approach to the theory of dispersion forces based on the quantum statistical mechanics of electromagnetic fluctuations in matter. It may be considered as a continuation of the method described in the previous section to the general case of continuous systems and finite temperatures.

The concept of relating van der Waals forces to electromagnetic fluctuations was conceived in Lifshitz's work [4]. Subsequently it was developed by Dzyaloshinskii, Lifshitz and Pitaevskii in 1961 [17] and extended and modified by several other workers; amongst them: Craig [18], Mitchell and Richmond [5] and Barash and Ginzburg [6].

The fluctuating microscopic electromagnetic field always exists in the matter; at finite temperature one can see an immediate effect of it: the thermal radiation. But even at zero temperature the fluctuations occur due to the quantum character of the field.

Dispersion interactions between various subsystems in an inhomogeneous medium arise because the fluctuating electromagnetic field in each of them is affected by the fields in the remaining parts.

In other words, there are correlations between the fluctuations in various points of the system; these correlations change as we move the subsystems apart or deform them. Now the correlation between fluctuations can be described in terms of macroscopic characteristics of the system; the so-called generalised susceptibilities. The formulation of this effect is a well-known result in statistical mechanics under the name of the fluctuation-dissipation theorem and which is due to Callen and Welton [19]. In particular, the correlation of electromagnetic fluctuations in equilibrium systems is described in terms of the dielectric and magnetic permittivities: $\underline{\underline{\varepsilon}}(\underline{r},\underline{r}';t,t')$ and $\underline{\underline{\mu}}(\underline{r},\underline{r}';t,t')$, respectively. In what follows we shall be concerned only with $\underline{\underline{\varepsilon}}(\underline{r},\underline{r}';t,t')$ and let $\underline{\underline{\mu}} = \underline{\underline{I}}$, since this is the case of all problems considered in this thesis. Let us mention, however, that the theory of van der Waals forces can readily be extended to the case of magnetic media, as has been shown by Ninham and Richmond [20].

The dielectric permittivity relates the macroscopic electric field to the polarisation induced by it in the medium; the polarization being the dipole moment per unit volume:

$$\underline{P}(\underline{r},t) = \frac{1}{4\pi}\int_{-\infty}^{t} dt' \int d^3\underline{r}' \,[\underline{\underline{\varepsilon}}(\underline{r},\underline{r}';t,t')-\delta(\underline{r}-\underline{r}')\delta(t-t')\underline{\underline{I}}\,]\,\underline{E}(\underline{r}',t') \,. \tag{1.53}$$

If the system was in equilibrium before applying the electric field $\underline{E}(\underline{r},t)$, the permittivity depends on the difference $t-t'$. Applying the time Fourier transform to both sides of eq (1.53) we obtain:

$$\underline{P}(\underline{r},\omega) = \frac{1}{4\pi}\int d^3\underline{r}' \,[\underline{\underline{\varepsilon}}(\underline{r},\underline{r}';\omega)-\delta(\underline{r}-\underline{r}')\underline{\underline{I}}]\,\underline{E}(\underline{r}',\omega) \tag{1.54}$$

where

$$\underline{\underline{\varepsilon}}(\underline{r},\underline{r}';\omega) = \int_{-\infty}^{+\infty} \theta(t)\underline{\underline{\varepsilon}}(\underline{r},\underline{r}',t)\exp(i\omega t)dt \,, \tag{1.55}$$

and $\underline{P}(\underline{r},\omega)$ and $\underline{E}(\underline{r},\omega)$ are the usual Fourier transforms of $\underline{P}(\underline{r},t)$ and $\underline{E}(\underline{r},t)$ respectively.

The dielectric permittivity $\underline{\underline{\varepsilon}}(\underline{r},\underline{r}';\omega)$ enters the macroscopic Maxwell's equations as follows:

$$\begin{aligned} \text{curl } \underline{E}(\underline{r},\omega) &= -\frac{i\omega}{c}\underline{B}(\underline{r},\omega) \\ \text{curl } \underline{B}(\underline{r},\omega) &= \frac{i\omega}{c}\int d^3\underline{r}\ \underline{\underline{\varepsilon}}(\underline{r},\underline{r}';\omega)\underline{E}(\underline{r}',\omega) + \frac{4\pi}{c}\underline{j}_{ext}(\underline{r},\omega) \end{aligned} \tag{1.56}$$

where $\underline{j}_{ext}(\underline{r},\omega)$ is the spectral form of some external current density. Introducing the potentials $\underline{A}(\underline{r},\omega)$ and $\phi(\underline{r},\omega)$ in the usual way:

$$\begin{aligned} \underline{E}(\underline{r},\omega) &= -\frac{i\omega}{c}\underline{A}(\underline{r},\omega) - \underline{\nabla}\phi(\underline{r},\omega) \\ \underline{B}(\underline{r},\omega) &= \text{curl } \underline{A}(\underline{r},\omega) \end{aligned} \tag{1.57}$$

we can transform Maxwell's equations (1.56) into the equations for the potentials. As it is well-known, there is a certain freedom in choosing the potentials (see, for example, Jackson [21]). We can, in particular, assume $\phi(\underline{r},\omega) \equiv 0$. In such a gauge Maxwell's equations for the vector potential $\underline{A}(\underline{r},\omega)$ take the form:

$$\frac{\omega^2}{c^2}\int \underline{\underline{\varepsilon}}(\underline{r},\underline{r}',\omega)\underline{A}(\underline{r}',\omega)d^3\underline{r}' - \text{curl curl } \underline{A} = -\frac{4\pi}{c}\underline{j}_{ext}(\underline{r},\omega)\ . \tag{1.58}$$

We shall also use the operator form of the above equation:

$$\underline{\underline{M}}\ \underline{A} = -\frac{4\pi}{c}\underline{j}_{ext} \tag{1.59}$$

where $\underline{\underline{M}}$ stands for the operation expressed by the l.h.s. of eq (1.56).

In a vacuum, eq (1.56) reduces to:

$$\frac{\omega^2}{c^2}\,\underline{A}(\underline{r}',\omega) - \text{curl}\,\text{curl}\,\underline{A} \;=\; -\frac{4\pi}{c}\,\underline{j}_{ext}(\underline{r},\omega) \quad , \tag{1.60}$$

or, in the symbolic operator form:

$$\underline{\underline{M}}^0\underline{A} \;=\; -\frac{4\pi}{c}\,\underline{j}_{ext} \quad . \tag{1.61}$$

The solution to eq (1.58) or (1.60) can be expressed by the dyadic Green's function $\underline{\underline{\mathcal{D}}}(\underline{r},\underline{r}',\omega)$ (or $\underline{\underline{\mathcal{D}}}^0(\underline{r},\underline{r}',\omega)$) which satisfies eq (1.58) ((1.60)) where we put $\underline{j}_{ext}(\underline{r},\omega) = -\underline{\underline{I}}\delta(\underline{r}-\underline{r}')$. Using the symbolic notation introduced above we may write:

$$\underline{\underline{M}}\;\underline{\underline{\mathcal{D}}} \;=\; \frac{4\pi}{c}\,\underline{\underline{I}}\delta(\underline{r}-\underline{r}') \tag{1.62}$$

and with a similar equation for $\underline{\underline{\mathcal{D}}}^0(\underline{r},\underline{r}',\omega)$. Once the Green's function $\underline{\underline{\mathcal{D}}}(\underline{r},\underline{r}',\omega)$ is known, the solution to eq (1.54) can be expressed as:

$$\text{a)}\quad \underline{A}(\underline{r},\omega) \;=\; -\int \underline{\underline{\mathcal{D}}}(\underline{r},\underline{r}'\omega)\underline{j}_{ext}(\underline{r}',\omega)d^3\underline{r}' \quad , \tag{1.63}$$

or symbolically

$$\text{b)}\quad \underline{A} \;=\; -\,\underline{\underline{\mathcal{D}}}\,\underline{j} \quad . \tag{1.63}$$

It will be convenient later to have yet another form of the equation for the dyadic Green's function $\underline{\underline{\mathcal{D}}}$. This form is known as Dyson's equation and is derived as follows. Rewriting operator $\underline{\underline{M}}$ as $\underline{\underline{M}} = \underline{\underline{M}} - \underline{\underline{M}}^0 + \underline{\underline{M}}^0$, and substituting this into eq (1.62) yields:

$$\underline{\underline{M}}^0\underline{\underline{\mathcal{D}}} = \frac{4\pi}{c}\underline{\underline{I}}\delta(\underline{r}-\underline{r}') - (\underline{\underline{M}}-\underline{\underline{M}}^0)\underline{\underline{\mathcal{D}}} \quad . \tag{1.64}$$

We can now find a formal solution to (1.64) by means of the vacuum Green's function $\underline{\underline{\mathcal{D}}}^0(\underline{r},\underline{r}',\omega)$, provided the r.h.s. of (1.64) is considered as a known function:

$$\underline{\underline{\mathcal{D}}} = \underline{\underline{\mathcal{D}}}^0 + \frac{c}{4\pi}\underline{\underline{\mathcal{D}}}^0(\underline{\underline{M}}-\underline{\underline{M}}^0)\underline{\underline{\mathcal{D}}} \quad . \tag{1.65}$$

Introducing the notation

$$\underline{\underline{\Pi}} = \frac{c}{4\pi}(\underline{\underline{M}} - \underline{\underline{M}}^0) \tag{1.66}$$

we arrive at Dyson's equation:

$$\underline{\underline{\mathcal{D}}} = \underline{\underline{\mathcal{D}}}^0 + \underline{\underline{\mathcal{D}}}^0\underline{\underline{\Pi}}\,\underline{\underline{\mathcal{D}}} \quad . \tag{1.67}$$

The operator $\underline{\underline{\Pi}}$ is called the polarization operator; the reason for this can be seen directly by comparing eq (1.53) with the actual form of $\underline{\underline{\Pi}}(\underline{r},\underline{r}',\omega)$:

$$\underline{\underline{\Pi}}(\underline{r},\underline{r}',\omega) = \frac{\omega^2}{4\pi c}[\underline{\underline{\varepsilon}}(\underline{r},\underline{r}',\omega) - \underline{\underline{I}}\delta(\underline{r}-\underline{r}')] \quad . \tag{1.68}$$

Next we shall give some general preliminaries from quantum statistical mechanics, which are necessary for the derivation of dispersion free energies.

1.4.2 Quantum statistical Green's functions

For completeness we shall quote some important results from quantum statistical mechanics which relate to the problems considered here. These

results include the properties of the quantum statistical Green's function, and can be found in most monographs dealing with statistical mechanics. In what follows we shall use the notation introduced by Zubarev [22]; all the standard results are taken from this monograph.

Consider a canonical ensemble of systems with the time independent Hamiltonian H. The ensemble is characterized by the density matrix

$$\rho_0 = \exp(-\beta H), \quad \beta = 1/kT \ . \tag{1.69}$$

The average equilibrium value of a quantity represented by the time independent operator A is given by the formula

$$\langle A \rangle_0 = \mathrm{Tr}(\rho_0 A)/\mathrm{Tr}\rho_0 \ . \tag{1.70}$$

Let us now introduce the time dependent retarded Green's function $G_{AB}(t)$ by the following definition:

$$G_{AB}(t) = -\frac{1}{i\hbar}\theta(t)\langle [A(t),B] \rangle_0 \tag{1.71}$$

where the brackets $[\,,]$ denote the commutator and the time dependence of the operator A (or B) is given by the canonical transformation

$$A(t) = \exp(iHt)A\exp(-iHt) \ . \tag{1.72}$$

It can be shown that the retarded Green's function has the usual meaning expressed in this case by the equation:

$$\langle A \rangle_t = \langle A \rangle_0 + G_{AB}(t) \tag{1.73}$$

where $\langle A \rangle_k$ is the average taken with respect to the density matrix $\rho(t)$ which satisfies the Liouville equation:

$$i\hbar \frac{\partial \rho}{\partial t} = [H - B\delta(t), \rho] \tag{1.74}$$

and the initial condition: $\rho(t)\Big|_{t<0} = \rho_0$. This interpretation of the retarded Green's function is very important since it enables us to relate the microscopic dynamic quantities to the macroscopic ones, as we shall see later. The retarded Green's function $G_{AB}(t)$ has its spectral form given by:

$$G_{AB}(\omega) = \int_{-\infty}^{+\infty} G_{AB}(t) \exp(i\omega t) dt \quad . \tag{1.75}$$

Let us also introduce the spectral intensity of the correlation function $\langle A(t)B \rangle_0$:

$$I_{AB}(\omega) = \int_{-\infty}^{+\infty} \exp(i\omega t) \langle A(t)B \rangle_0 \quad . \tag{1.76}$$

It can be shown that the spectral form of the Green's function (1.75) can be expressed in terms of the spectral intensity $I_{AB}(\omega)$:

$$G_{AB}(\omega) = \int_{-\infty}^{+\infty} (1 - \exp(-\beta\hbar\omega)) I_{AB}(\omega) \frac{d\omega'}{(\omega - \omega' + i\gamma)} \tag{1.77}$$

where $\gamma > 0$ symbolically denotes the path of integration near the singularity $\omega = \omega'$. One can write the inverse expression to eq (1.77):

$$\mathrm{Im} G_{AB}(\omega) = -\frac{1}{2\hbar} (1 - \exp(-\beta\hbar\omega)) I_{AB}(\omega) \tag{1.78}$$

provided the intensity $I_{AB}(\omega)$ is real. This will always be the case

when the operators $A(t)$ and $B(t)$ are time reversible with the same polarity, i.e. $A(-t) = \mu A(t)$ and $B(-t) = \mu B(t)$, where $\mu = \pm 1$. We mention here, that in the case of electromagnetic interactions this condition is fulfilled since, for instance, the current density and the vector potential both change the sign under time reversal. From eq (1.78) we can write the following expression for the equilibrium average value of the product AB:

$$< AB >_0 = \frac{1}{2\pi} \int_{-\infty}^{+\infty} I_{AB}(\omega) d\omega = -\frac{\hbar}{\pi} \int_{-\infty}^{+\infty} \frac{\mathrm{Im} G_{AB}(\omega)}{1-\exp(-\beta\omega)} \quad . \tag{1.79}$$

We shall transform the above equation to the more frequently used form involving the summation over the imaginary frequencies $i\xi_n = (2\pi n/\beta\hbar)i$, $n = 0,1,\ldots,$. We note that the Green's function $G_{AB}(\omega)$ has the following symmetry properties:

$$\begin{aligned} &\text{a)} \quad \mathrm{Re} G_{AB}(-\omega) = \mathrm{Re} G_{AB}(\omega) \\ &\text{b)} \quad \mathrm{Im} G_{AB}(-\omega) = -\mathrm{Im} G_{AB}(\omega) \qquad \text{if } A = A^{\dagger},\ B = B^{\dagger} \end{aligned} \tag{1.80}$$

where $(\dagger)$ denotes the Hermitian conjugation. The above properties follow from the fact that the time dependent Green's function for Hermitian operators is real. Also, because $G_{AB}(\omega)$ is analytic for $\mathrm{Im}\,\omega > 0$ and vanishes faster than $1/|\omega|$ for $|\omega| \to \infty$ (Zubarev, [22]), it follows that

$$G_{AB}(\omega) = \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{G_{AB}(\omega')}{\omega' - \omega} d\omega', \quad \mathrm{Im}\,\omega > 0 \quad . \tag{1.81}$$

After letting $\omega = i\xi$, $\xi > 0$, in the above equation it becomes evident from eqs (1.80) that $\mathrm{Im} G_{AB}(i\xi) = 0$. In addition one can easily prove the following identity (cf. eq (1.50)):

$$G_{AB}(i\xi) = -\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{G_{AB}(\omega)}{\omega^2+\xi^2} = -\frac{1}{\pi}\int_{-\infty}^{+\infty}\frac{\omega \mathrm{Im}G_{AB}(\omega)}{\omega^2+\xi^2} \quad . \tag{1.82}$$

Therefore we can transform the integral of (1.79) as follows (Mitchell and Richmond [5]):

$$-\frac{\hbar}{\pi}\int_{-\infty}^{+\infty}\frac{\mathrm{Im}G_{AB}(\omega)}{1-\exp(-\beta\hbar\omega)} = -\frac{2\hbar}{\pi}\int_{0}^{\infty}\mathrm{Im}G_{AB}(\omega)\coth\left(\frac{\beta\hbar\omega}{2}\right) = -\frac{2}{\beta}\sum_{n=0}^{\infty}{}' G_{AB}(i\xi_n) \tag{1.83}$$

where we have used the expansion:

$$\coth\left(\frac{\beta\hbar\omega}{2}\right) = \frac{4}{\beta\hbar}\sum_{n=0}^{\infty}{}'\frac{\omega}{\omega^2+\xi_n^2}, \qquad \xi_n = \frac{2\pi m}{\beta\hbar} \quad . \tag{1.84}$$

Finally then we can write:

$$\langle AB \rangle_0 = -\frac{2}{\beta}\sum_{n=0}^{\infty}{}' G_{AB}(i\xi_n) \tag{1.85}$$

which will be the starting point in the following application.

1.4.3 Dispersion free energies

In a similar way to that adopted in the previous section, we shall use the coupling parameter formalism in order to calculate the free energy in the system due to electromagnetic interactions. Let H_1 be that part of the total Hamiltonian which accounts for these interactions and let H_0 be the remaining part of it. Introducing a fictitious Hamiltonian $H(\lambda)$:

$$H(\lambda) = H_0 + \lambda H_1 \tag{1.86}$$

we can derive the expression for the free energy due to the interactions

represented by H_1 [5,6]:

$$\Delta F = \int_0^1 \frac{d\lambda}{\lambda} < \lambda H_1 >_\lambda \tag{1.87}$$

where the subscript on the average sign means that the average is taken with respect to the density matrix:

$$\rho(\lambda) = \exp(-\beta H(\lambda)). \tag{1.88}$$

For a system of charged particles (electrons and nuclei) interacting with each other through the equilibrium electromagnetic field the Hamiltonian H_1 is:

$$H_1 = -\frac{1}{2c} \sum_{\nu=1}^{3} \int d^3\underline{r}\, A^\nu(\underline{r}) j^\nu(\underline{r}) \tag{1.89}$$

where $A^\nu(\underline{r})$ and $j^\nu(\underline{r})$ are the components of the vector potential and the current density operators, respectively. Here we have assumed that the gauge of the potentials is such that $\phi = 0$. The interpretation of the Green's function $G_{jA}^{\mu\nu}(\underline{r},\underline{r}';t)$ can now be seen from eq (1.73). Indeed, substituting in this equation the value of the current density component $j^\mu(\underline{r})$ in place of A and the value of the vector potential component divided by the velocity of light, c, $\frac{1}{c} A^\nu(\underline{r}')$ in place of B, we find that the Green's function is the average current density at point $\underline{r}$ due to an impulsive force which produces the energy input to the system: $-\frac{1}{c} A^\nu(\underline{r}')\delta(t)$. Note that $< \underline{j}(\underline{r}) >_0 = 0$ as the system is in equilibrium. According to eq (1.87) this energy input can be achieved by introducing an external current source $j_{ext}(\underline{r},t) = \delta(\underline{r}-\underline{r}')\delta(t)$. In other words the Green's function $G_{jA}^{\mu\nu}(\underline{r},\underline{r}',t)$ is the current-current response function describing the macroscopic polarization current density

at $\underline{r}$ due to an external current impulse at $\underline{r}'$. In the general case the evaluation of this response function is not trivial and several approximate methods have been developed including the diagrammatic technique, hierarchy of equations, etc. [23,24]. For dielectric materials, however, we can apply the approximation of linear classical electrodynamics. This can be expressed as the assumption that the average current density $<\underline{j}>$ depends linearly on the average vector potential $<\underline{A}>$:

$$<\underline{j}(\underline{r},t)> = \int_{-\infty}^{t} dt' \int d^3\underline{r}' \; \underline{\underline{\Pi}}(\underline{r},\underline{r}',t,t') <\underline{A}(\underline{r}',t')> \quad (1.90)$$

or symbolically:

$$<\underline{j}> = \underline{\underline{\Pi}} <\underline{A}> \quad . \quad (1.91)$$

The averaging of the microscopic Maxwell's eqs:

$$\underline{\underline{M}}^0 \underline{A} = -\frac{4\pi}{c}\underline{j} - \frac{4\pi}{c}\underline{j}_{ext} \quad (1.92)$$

leads on one hand to the macroscopic Maxwell's equations given by eq (1.59), and on the other to

$$\underline{\underline{M}}^0 <\underline{A}> = -\frac{4\pi}{c}<\underline{j}> - \frac{4\pi}{c}\underline{j}_{ext} \; . \quad (1.93)$$

Combining eqs (1.93), (1.59) and (1.91) we see immediately that the operator $\underline{\underline{\Pi}}$ of eq (1.91) is the same as the polarization operator $\underline{\underline{\Pi}}$ introduced in eq (1.66). We may say, therefore, that as long as the approximation of the linear classical electrodynamics is valid, the current-current response function $\underline{\underline{G}}_{jA}(\underline{r},\underline{r}',t)$ can be expressed by the macroscopic Green's dyadic $\underline{\underline{\mathcal{D}}}(\underline{r},\underline{r}',t)$ (cf. eqs (1.63) and (1.91))

in the following way:

$$\underline{\underline{G}}_{jA} \equiv \underline{\underline{\Pi}}\,\underline{\underline{\mathcal{D}}} \tag{1.94}$$

where we have used the operator notation.

We now come back to the expression for the free energy (1.87). Upon substituting into it the form of the Hamiltonian from eq (1.89) and using the general result relating the correlation function to the quantum Green's function (1.85) with the suitable substitution, we arrive at the expression:

$$\Delta F = -\frac{1}{\beta} \sum_{n=0}^{\infty}{}' \sum_{\mu=1}^{3} \int d^3\underline{r} \int_0^1 \frac{d\lambda}{\lambda} G_{jA}^{\mu\nu}(\underline{r},\underline{r},i\xi_n,\lambda) \quad . \tag{1.95}$$

This equation can also be written in the following form obtained by using eq (1.94):

$$\Delta F = -\frac{1}{\beta} \sum_{n=0}^{\infty}{}' \int_0^1 \frac{d\lambda}{\lambda} \mathrm{Tr}\underline{\underline{\Pi}}(\lambda,i\xi_n)\underline{\underline{\mathcal{D}}}(\lambda,i\xi_n) \quad . \tag{1.96}$$

We shall now discuss the dependence of the polarization kernel $\underline{\underline{\Pi}}$ and the dyadic Green's function $\underline{\underline{\mathcal{D}}}(\lambda,i\xi)$ on the coupling parameter λ. Firstly, note that for $\lambda=0$ the electromagnetic interactions in the system are switched off and hence the polarization operator equals zero. The electromagnetic Green's function $\underline{\underline{\mathcal{D}}}(0,i\xi_n)$ becomes equal to that of a vacuum - $\underline{\underline{\mathcal{D}}}^0(i\xi_n)$. For $\lambda=1$, the polarization operator assumes the form given by eq (1.58) and the Green's function $\underline{\underline{\mathcal{D}}}$ becomes that of the real system. For arbitrary $0 \leqslant \lambda \leqslant 1$ the $\underline{\underline{\mathcal{D}}}(\lambda,i\xi_n)$ obeys Dyson's equation:

$$\underline{\underline{\mathcal{D}}} = \underline{\underline{\mathcal{D}}}^0 + \underline{\underline{\mathcal{D}}}^0\underline{\underline{\Pi}}(\lambda)\underline{\underline{\mathcal{D}}}(\lambda) \tag{1.97}$$

whose formal solution can be written as:

$$\underline{\underline{\mathcal{D}}}(\lambda) = (\underline{\underline{I}} - \underline{\underline{\mathcal{D}}}^0\underline{\underline{\Pi}}(\lambda))^{-1}\underline{\underline{\mathcal{D}}}^0 \tag{1.98}$$

Differentiating eq (1.97) with respect to λ yields:

$$\underline{\underline{\mathcal{D}}}'(\lambda) = \underline{\underline{\mathcal{D}}}^0\underline{\underline{\Pi}}'(\lambda)\underline{\underline{\mathcal{D}}}(\lambda) + \underline{\underline{\mathcal{D}}}^0\underline{\underline{\Pi}}(\lambda)\underline{\underline{\mathcal{D}}}'(\lambda) \tag{1.99}$$

the solution of which is:

$$\underline{\underline{\mathcal{D}}}'(\lambda) = (\underline{\underline{1}} - \underline{\underline{\mathcal{D}}}^0\underline{\underline{\Pi}}(\lambda))^{-1}\underline{\underline{\mathcal{D}}}^0\underline{\underline{\Pi}}'(\lambda)\underline{\underline{\mathcal{D}}}(\lambda) = \underline{\underline{\mathcal{D}}}(\lambda)\underline{\underline{\Pi}}'(\lambda)\underline{\underline{\mathcal{D}}}(\lambda) \tag{1.100}$$

where the last equality follows from eq (1.94). If we approximate the λ dependence of the polarization operator by

$$\underline{\underline{\Pi}}(\lambda) = \lambda\underline{\underline{\Pi}}(1) \tag{1.101}$$

then, as has been shown by Davies [25], we obtain from (1.100) and (1.96)

$$\Delta F = -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' \mathrm{Tr}\int_0^1 d\lambda\underline{\underline{\mathcal{D}}}^{-1}(\lambda,i\xi_n)\underline{\underline{\mathcal{D}}}(\lambda,i\xi_n) = -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' \mathrm{Tr}\log[\underline{\underline{\mathcal{D}}}(i\xi_n)(\underline{\underline{\mathcal{D}}}^0)^{-1}] \tag{1.102}$$

$$= -\frac{1}{\beta}\sum_{n=0}^{\infty} \mathrm{Tr}\log(\underline{\underline{I}} + \underline{\underline{G}}(i\xi_n))$$

In the above equation the last step follows from the identity

$$(\underline{\underline{\mathcal{D}}}^0)^{-1}\underline{\underline{\mathcal{D}}} = \underline{\underline{1}} + \underline{\underline{\Pi}}\,\underline{\underline{\mathcal{D}}} = \underline{\underline{1}} + \underline{\underline{G}} \tag{1.103}$$

where we omitted the subscripts j and A in the current-current response function $\underline{\underline{G}}$.

Applying in (1.102) the Fredholm expansion:

$$\mathrm{Tr}\log(\underline{\underline{I}}+\underline{\underline{B}}) = \sum_{n=1}^{\infty}\frac{(-1)^{n+1}}{n}\mathrm{Tr}\underline{\underline{B}}^{n} \tag{1.104}$$

we obtain for the free energy:

$$\Delta F = -\frac{1}{\beta}\sum_{n=0}^{\infty}{}'\sum_{\ell=1}^{\infty}\frac{(-1)^{\ell+1}}{\ell}\mathrm{Tr}\left[\underline{\underline{G}}(i\xi_n)\right]^{\ell} . \tag{1.105}$$

We shall apply now eq (1.105) in deriving the energy density of a homogeneous dielectric medium. This exercise will enable us to take a closer look at the limitations involved in the above derivation. In a homogeneous dielectric the macroscopic current-current response function is equal to the dipole-dipole response function which, in the nonretarded approximation ($c \to \infty$), can be written as:

$$\underline{\underline{G}}(\underline{r},\underline{r}',\omega) = \left\{\int\frac{d^3k}{(2\pi)^3}\frac{\varepsilon(\underline{k},\omega)-1}{4\pi\varepsilon(\underline{k},\omega)}\cdot\frac{k_i k_j}{k^2}e^{-i\underline{k}\cdot(\underline{r}-\underline{r}')}\right\} \tag{1.106}$$

Substituting the above equation into (1.105) and retaining the leading term we obtain:

$$\Delta F = -\frac{1}{\beta}\int d^3\underline{r}\sum_{n=0}^{\infty}{}'\int\frac{d^3k}{(2\pi)^3}\frac{\varepsilon(\underline{k},i\xi_n)-1}{4\pi\varepsilon(\underline{k},i\xi_n)} . \tag{1.107}$$

In the case when the dielectric susceptibility does not depend on $\underline{k}$, the integral with respect to this variable diverges. Therefore, accounting for the spatial dispersion of the dielectric susceptibility at small distances is crucial if one wants to calculate the energy density of a bulk dielectric.

Now let us introduce a sharp cut-off wave number k_c, by saying that for the electric field with wavelength shorter than $2\pi/k_c$

the dielectric constant becomes that of a vacuum, i.e. $\varepsilon=1$. Below the cut-off let ε be constant different from 1 and independent of $\underline{k}$. Thus from eq (1.107) we obtain:

$$\Delta F/\text{unit volume} \approx -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' \frac{\varepsilon(i\xi_n)-1}{3a^3\varepsilon(i\xi_n)} \tag{1.108}$$

where $a = 2\pi/k_c$. In low density dielectrics, such as gases, one makes the usual approximation:

$$\varepsilon(\omega) = 1 + 4\pi n\alpha(\omega), \quad 4\pi n\alpha(\omega) << 1 \tag{1.109}$$

where n is the density number and $\alpha(\omega)$ the polarizability of the constituent molecules. Substituting (1.109) into (1.108), and dividing by the density number n we obtain the energy of the dielectric per molecule:

$$\Delta F/\text{molecule} = -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' \frac{4}{3}\frac{\pi}{a^3}\frac{\alpha(i\xi_n)}{\varepsilon(i\xi_n)} \quad . \tag{1.110}$$

This compares with the expression for the self-energy of a molecule in a dielectric medium introduced by Mahanty and Ninham [26]:

$$E_s = -\frac{4}{\pi^{\frac{1}{2}}(a')^3}\sum_{n=0}^{\infty}{}' \frac{\alpha(i\xi_n)}{\varepsilon(i\xi_n)} \tag{1.111}$$

where a' is the size of the molecule. Comparing (1.110) with (1.111) we see that the cutoff wavelength a relates to the molecular size a' as approximately $a = 1.23a'$. If we note also that a' (Mahanty and Ninham [26]) is somewhat smaller than the van der Waals radius and a is the measure of an assumed Gaussian spread of the polarizability, we conclude that the cutoff wavelength can be taken as the molecular radius.

We can say, therefore, that the dispersion energy of the bulk dielectric can be considered as the sum of the self-energies of the constituent molecules. These self-energies include the many-body effect of interaction between the molecules, since this interaction is reflected in the dielectric susceptibility of the medium.

We shall now discuss briefly the validity of the assumption expressed by eq (1.101) which lead to the result for the dispersion free energy (1.102). The λ dependence of the polarization operator is determined at the moment we choose the division of the total Hamiltonian of the system into the "interesting" - H_1 and the "uninteresting" - H_0 part. Indeed, the λ dependence of all averages is determined by the form of the Hamiltonian $H(\lambda) = H_0 + \lambda H_1$. The question now arises as to what division of the total Hamiltonian leads to the linear dependence of the polarization kernel on the coupling parameter. Barash and Ginzburg [6] provide an argument that on choosing as H_1 the long wavelength part of the interactions through the equilibrium electromagnetic field it is possible to write $\Pi(\lambda) = f(\lambda)\cdot\Pi(1)$, where $f(\lambda)$ is a scalar factor depending on λ, and $\Pi(1)$ is the polarization operator in the real system.*

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* There is some confusion in their paper caused by their form of the interaction Hamiltonian H_1. Specifically, they omit the factor of 1/2 as compared with that form of the Hamiltonian given in eq (1.89) and which is normally used whenever two-body interaction is concerned. On the other hand they wish to arrive at the equation expressed here by (1.102) which is equivalent to the classical Lifshitz result (Dzyaloshinskii *et al* [17]). Therefore, they use the following dependence on λ of the polarization operator: $\Pi(\lambda) = \lambda^2\Pi(1)$, which, upon substituting into Dyson's equation and performing operations similar to those given in eqs (1.97)-(1.100) leads to the cancellation of 2 and the correct expression.

The choice $f(\lambda) = \lambda$ is the simplest and leads to the results established earlier [17]. The assumption underlying their argument was that the dielectric properties of the medium are determined by the short-range intermolecular forces, hence remain unchanged as the long-range part of the interactions is switched on.

One may question the validity of this assumption (even for spatially non-dispersive media) in calculating bulk energies. Below we consider an example which shows that in such a case letting $\Pi(\lambda) = \lambda\Pi(1)$ is equivalent to the low density approximation (1.109). The long-wavelength limit corresponds to considering only the dipole-dipole interactions between molecules. As we have seen in Section 3, the coupling constant can then be introduced on the macroscopic level by replacing the polarizability of the molecules, α, through $\lambda\alpha$. Suppose that the molecular polarizability is related to the dielectric constant of the medium by the Clausius-Mossoti equation

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{4}{3}\pi n\alpha \equiv \kappa \,. \tag{1.112}$$

Introducing in (1.112) the parameter λ and calculating the polarization $\underline{\underline{\Pi}}$ we obtain:

$$\underline{\underline{\Pi}}(\lambda) = \frac{3}{4\pi}\frac{\kappa\lambda}{(1-\kappa\lambda)}\underline{\underline{I}} = \frac{\varepsilon-1}{4\pi}\underline{\underline{I}} \,. \tag{1.113}$$

Substituting (1.113) into eq (1.96) we obtain

$$\Delta F = -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' \int d^3\underline{r} \int_{|\underline{k}|\leq k_c} \frac{d^3\underline{k}}{(2\pi)^3}\int_0^\lambda \frac{d\lambda}{\lambda}\frac{\varepsilon(\lambda,i\xi_n)-1}{4\pi\varepsilon(\lambda,i\xi_n)} \tag{1.114}$$

$$= -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' \int d^3\underline{r}\,\frac{1}{3a^3}\,\frac{3}{2}\log(2\kappa(i\xi_n)+1) \,,$$

where, as in eq (1.108), $a = 2\pi/k_c$. Bearing in mind that κ is given by eq (1.112) and expanding the log term in the above equation to the leading term we obtain:

$$\Delta F/\text{unit volume} = -\frac{1}{\beta} \sum_{n=0}^{\infty}{}' \frac{1}{a^3} \frac{\varepsilon(i\xi_n)-1}{\varepsilon(i\xi_n)+2} \tag{1.115}$$

which is equivalent to (1.108) provided we can write approximately:

$$\frac{3\varepsilon}{\varepsilon+2} \approx 1 . \tag{1.116}$$

As we have shown then, more rigorous approaches based on the Clausius-Mossoti equation yield other than a dependence of the polarization operator $\underline{\underline{\Pi}}$ proportional to λ, and only in the limit $\varepsilon \approx 1$ do we obtain an equivalence to the result eq (1.108) for the bulk energy density. This example illustrates only a fraction of the difficulties one encounters in calculating bulk energies.

Let us observe that one cannot separate meaningfully the long-wavelength interaction in H_1 leaving at the same time the short-wavelength part in H_0. Indeed, since there is no physical "strength" constant distinguishing these parts, the switching on of the dipole-dipole interactions is intimately connected with doing the same with dipole-quadrupole, quadrupole-quadrupole, etc. Therefore, whenever higher order multipole interactions are significant one has to calculate the dispersion-free energy including these interactions in H_1, otherwise the free energy expression will not be meaningful beyond terms of order e^2, i.e. the low density limit. This, unfortunately, leads to a complicated functional dependence of the polarization operator on λ, and to our knowledge this problem has not been resolved yet. This defect is implicit (although in disguised form) in *all* treatments of van der Waals interactions.

The situation is much better in the case of interaction between two separate bodies, i.e. when the bodies have sharp, well-defined boundaries. There, one can separate the total Hamiltonian into the parts concerning the isolated bodies plus the interaction Hamiltonian between them. We shall examine this procedure in the example of a single molecule interacting with a dielectric halfspace.

The system, therefore, consists of a single molecule, characterized by its polarizability α and a dielectric halfspace B. The total Hamiltonian can be written as

$$H = H_0 - \underline{P} \cdot \underline{E} \tag{1.117}$$

where $\underline{P}$ is the dipole moment operator of the molecule. Introduction of the parameter λ into the Hamiltonian can be absorbed by letting the elementary charge in the molecule become: $e' = \lambda e$. This means that the polarizability $\alpha(\lambda)$ is proportional to λ^2, as it is proportional to $(e')^2$. According to eq (1.85) the mean value of the interaction Hamiltonian $H_1 = -\underline{P} \cdot \underline{E}$ is expressed in terms of the Green's function $G^{\mu\nu}_{\underline{P}\,\underline{E}}(i\xi)$ as

$$\langle \underline{P} \cdot \underline{E} \rangle = -\frac{2}{\beta} \sum_{n=0}^{\infty}{}' \operatorname{Tr} \underline{\underline{G}}_{\underline{P}\,\underline{E}}(i\xi_n) \ . \tag{1.118}$$

The dyadic $\underline{\underline{G}}_{\underline{P}\,\underline{E}}$ can be interpreted as the dipole-dipole response taken at $\underline{r}_0$, $\underline{\underline{G}}(\underline{r}_0,\underline{r}_0,i\xi)$, where $\underline{r}_0$ is the position of the molecule. The dyadic $\underline{\underline{G}}(\underline{r},\underline{r}',i\xi)$ is related to the electric field dyadic (dipole-field) $\underline{\underline{\mathcal{D}}}(\underline{r}_0,\underline{r},i\xi)$ by

$$\underline{\underline{G}}(\underline{r}_0,\underline{r}';i\xi) = \alpha(i\xi)\underline{\underline{\mathcal{D}}}(\underline{r}_0,\underline{r}';i\xi) \ . \tag{1.119}$$

On the other hand the electric field dyadic at any point $\underline{r}$ outside B

satisfies the equation

$$\underline{\underline{\mathcal{D}}}(\underline{r},\underline{r}',i\xi) = \underline{\underline{\mathcal{D}}}^0_B(\underline{r},\underline{r}',i\xi) - \underline{\underline{\mathcal{D}}}^0_B(\underline{r},\underline{r}_0,i\xi)\alpha(i\xi)\underline{\underline{\mathcal{D}}}(\underline{r}_0,\underline{r}',i\xi) \tag{1.120}$$

where $\underline{\underline{\mathcal{D}}}^0_B$ is the electric field dyadic in the absence of the molecule. Obtaining the formal solution of eq (1.120) and inducing the coupling parameter dependence through the substitution $\alpha \to \lambda^2\alpha$ we can show the following identity:

$$\underline{\underline{G}}(\underline{r}_0,\underline{r}_0,i\xi,\lambda) = \frac{\lambda}{2}\frac{\partial}{\partial\lambda}\log(\underline{\underline{I}} + \lambda^2\alpha(i\xi)\underline{\underline{\mathcal{D}}}^0_B(\underline{r}_0,\underline{r}_0,i\xi)) \ . \tag{1.121}$$

The free energy of interaction between the molecule and the dielectric is obtained by the coupling constant integration (cf. (1.87)):

$$\Delta F = - \int_0^1 \frac{d\lambda}{\lambda} < \underline{P}(\lambda)\cdot\underline{E}(\lambda) > \tag{1.122}$$

which, from eqs (1.118) and (1.121) gives the final result:

$$\Delta F = -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' \mathrm{Tr}\log(\underline{\underline{I}} + \alpha(i\xi_n)\underline{\underline{\mathcal{D}}}^0_B(\underline{r}_0,\underline{r}_0;i\xi_n)) \ . \tag{1.123}$$

Eq (1.123) might be obtained otherwise directly from eq (1.102), if we specialized it to the present example.

Equation (1.102) is also equivalent to eq (1.3) which has been derived from the normal mode analysis. To see this equivalence one has to interpret properly the secular determinant of eq (1.1): we refer here to Barash and Ginzburg [6] for details. The normal mode method is, therefore, equivalent to the fluctuation-dissipation method provided the assumption of linearity of the polarization operator with respect to λ (or λ^2, as the case may be) is valid. We have shown that this is the

case when we are concerned with the interaction between bodies with sharp boundaries, but it fails when applied, for instance, in calculating bulk energies. It appears also that a similar limitation of the van Kampen theory exists when the bodies are so close, that the correlation between bulk currents in each of them has to be taken into account [27].

In any case, a conclusion can be drawn that there does exist a relation between the properties of the macroscopic Green's function for Maxwell's equations and the dispersion free energies in the system. The problems of van der Waals interactions are reduced to electromagnetic problems and it is possible to make use of the wealth of electromagnetic techniques in solving them.

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CHAPTER 2

INTERACTION BETWEEN MOLECULES IN THE PRESENCE OF MACROSCOPIC BODIES

2.1 Introduction

The problem of the influence of a macroscopic body (substrate) on interaction between atoms and molecules has long attracted attention because of its importance for the understanding of adsorption and catalysis. The problem in general is difficult, especially in catalysis where the presence of the substrate affects chemical bonds between atoms. The simplest possible case is when the interacting molecules are sufficiently far from the substrate and from each other; then the interaction forces are long-range of electrostatic or van der Waals type. In this chapter we deal with the effect of the substrate on van der Waals forces. The results obtained here will be used in the next chapter where we discuss dispersion forces in physical adsorption.

Some approaches to the problem have been based on semi-empirical considerations where one introduces to the interaction potential parameters whose values are determined from experimental data. These methods and also some theoretical models have been reviewed by Everett [1]. McLachlan [2] was the first to apply dispersion force theory to the problem of substrate mediated interactions in the case when the molecules were in a vacuum near a dielectric halfspace. A more general problem of the molecules interacting near the interface between two dielectric semi-infinite media has been considered by Richmond and Sarkies [3] . This work was the first in which the normal mode theory of dispersion interactions had been applied in this area. When the molecules are in a confined space, such as a pore or a cavity, the van der Waals forces

between them are affected even more strongly than near a plane surface. Calculations of this effect have been made by Mahanty and Ninham [4,5] for molecules in a dielectric layer between semi-infinite dielectric media, and in a gap between two conducting planes. A generalization of their approach has been done by Olds [6] for the case of a rectangular infinite duct with perfectly conducting walls.

We begin this chapter with a general formulation for calculating the substrate effects on the interaction between molecules. The novelty in this approach is making a clear distinction between those effects, which are due to reflected, or induced electric fields, and the unaffected part of the interaction, which is the same as in free space. We apply the general expressions to the case when the substrate is a dielectric halfspace, and recover McLachlan's [2] results as a special case. In the last section, we consider the effects of spatially dispersive media on molecular forces.

2.2 A general formulation

Consider a body B and two molecules at positions $\underline{R}_1$, $\underline{R}_2$ outside B. For simplicity assume that the molecules are characterized by isotropic polarizabilities $\alpha_1(\omega)$, $\alpha_2(\omega)$ of the form:

$$\alpha_i(\omega) = \frac{\alpha_{0i}}{1 - \frac{\omega^2}{\omega_{0i}^2}} \quad , \qquad i = 1,2 \tag{2.1}$$

where ω_{0i} are the main absorption frequencies of the molecules (typically $\omega_{0i} = 2 \times 10^{16}\ s^{-1}$) and α_{0i} are their static polarizabilities.

Whenever the distances between the parts of the system are much smaller than $\lambda_{0i} = 2\pi c/\omega_{0i}$ (typically $\lambda_{0i} \approx 500$ Å) we can use the nonretarded a-proximation, that is the limiting form of the theory

obtained by letting the velocity of light $c \to \infty$.

An oscillating dipole $\underline{p}e^{-i\omega t}$ at the position $\underline{R}'$ outside B creates an electric field whose value at any point $\underline{R}$ also outside B is related to the source through the dyadic Green's function $\underline{\underline{\mathcal{D}}}_B(\underline{R},\underline{R}',\omega)$. The addition of the two molecules is equivalent to the addition of two polarizable dipoles to the system. The electric field can now be represented by the equation:

$$\underline{E}(\underline{R}) = \underline{\underline{\mathcal{D}}}_B(\underline{R},\underline{R}')\underline{p} + \sum_{i=1}^{2} \underline{\underline{\mathcal{D}}}_B(\underline{R},\underline{R}_i)\alpha_i \underline{E}(\underline{R}_i) \tag{2.2}$$

where we have suppressed, for notational convenience, the ω dependence. Letting $\underline{R} = \underline{R}_1$ and then $\underline{R} = \underline{R}_2$ in eq (2.2) we obtain the system of algebraic equations for the field $\underline{E}$ acting on the molecules. The secular determinant of this system can readily be obtained:

$$D = \begin{vmatrix} \underline{\underline{I}} - \alpha_1 \underline{\underline{\mathcal{D}}}_B(\underline{R},\underline{R}) & \alpha_2 \underline{\underline{\mathcal{D}}}_B(\underline{R}_1,\underline{R}_2) \\ \alpha_1 \underline{\underline{\mathcal{D}}}_B(\underline{R}_2,\underline{R}_1) & \underline{\underline{I}} - \alpha_2 \underline{\underline{\mathcal{D}}}_B(\underline{R}_2,\underline{R}_2) \end{vmatrix} . \tag{2.3}$$

By equating the determinant D to zero we get the dispersion equation, from which the frequencies of the modes supported by the system can be found. The free energy associated with these modes can be written as (cf. eq (1.3) of Chapter 1):

$$F = \frac{1}{\beta} \sum_{n=0}^{\infty}{}' \log D(i\xi_n) , \quad \xi_n = 2\pi n/\beta . \tag{2.4}$$

The free energy is a certain function of the positions $\underline{R}_1$ and $\underline{R}_2$ of the molecules, through the secular determinant D (eq (2.3)). We wish

to separate from F the terms corresponding to the free energies of interaction between single molecules and B; what is left is the mutual interaction between the molecules. In other words we seek to decompose the free energy as

$$F(\underline{R}_1,\underline{R}_2|\alpha_1,\alpha_2) = F_1(\underline{R}_1|\alpha_1) + F_2(\underline{R}_2|\alpha_2) + F_{12}(\underline{R}_1,\underline{R}_2|\alpha_1,\alpha_2). \quad (2.5)$$

The above decomposition can be achieved by a trick due to Mahanty and Ninham [7] which in this particular case reduces to the following transformation of the log term in (2.4):

$$\begin{aligned} \log D = {} & \log|\underline{\underline{I}} - \alpha_1\underline{\underline{\mathcal{D}}}_B(\underline{R}_1,\underline{R}_1)| + \log|\underline{\underline{I}} - \alpha_2\underline{\underline{\mathcal{D}}}_B(\underline{R}_2,\underline{R}_2)| \\ & + \log|\underline{\underline{I}} - \alpha_1\alpha_2\underline{\underline{\mathcal{D}}}_B(\underline{R}_1,\underline{R}_2)\underline{\underline{\mathcal{D}}}_B(\underline{R}_2,\underline{R}_1)| \quad . \end{aligned} \quad (2.6)$$

Let us introduce the spectral densities of the free energies

$$U_k(\underline{R}_k,i\xi) = \log|\underline{\underline{I}} - \alpha_k(i\xi)\underline{\underline{\mathcal{D}}}_B(\underline{R}_k,\underline{R}_k)| \quad , \qquad k = 1,2 \quad (2.7)$$

$$U_{12}(\underline{R}_1,\underline{R}_2,i\xi) = \log|\underline{\underline{I}} - \alpha_1(i\xi)\alpha_2(i\xi)\underline{\underline{\mathcal{D}}}_B(\underline{R}_1,\underline{R}_2,i\xi)\underline{\underline{\mathcal{D}}}_B(\underline{R}_2,\underline{R}_1,i\xi)|. \quad (2.8)$$

With this notation we can write:

$$F_k(\underline{R}_k) = \frac{1}{\beta}\sum_{n=0}^{\infty}{}' U_k(\underline{R}_k,i\xi_n) \qquad k = 1,2 \quad (2.9)$$

$$F_{12}(\underline{R}_1,\underline{R}_2) = \frac{1}{\beta}\sum_{n=0}^{\infty}{}' U_{12}(\underline{R}_1,\underline{R}_2,i\xi_n) \quad . \quad (2.10)$$

In most cases the dependence of the above expressions for the free energies on the geometry of the system, i.e. on the positions of the molecules with respect to B and each other can be seen at the level of

the spectral densities. We shall now derive approximate forms of these densities by using the Fredholm identity:

$$\log|\underline{\underline{I}} - \underline{\underline{A}}| = -\sum_{n=1}^{\infty} \frac{1}{n} \mathrm{Tr}\, \underline{\underline{A}}^n \,. \tag{2.11}$$

Applying this equation in (2.7) and (2.8) and retaining the leading terms we obtain

$$U_k = -\alpha_k \mathrm{Tr}\, \underline{\underline{\mathcal{D}}}_B(\underline{R}_k, \underline{R}_k) \,, \quad k = 1,2 \tag{2.12}$$

$$U_{12} = -\alpha_1\alpha_2 \mathrm{Tr}\, \{\underline{\underline{\mathcal{D}}}_B(\underline{R}_1, \underline{R}_2)\underline{\underline{\mathcal{D}}}_B(\underline{R}_2, \underline{R}_1)\} \,. \tag{2.13}$$

Since we did not take into account the finite size of the molecules, the energies of interaction between single molecules and B contain their infinite self-energies; thus eqs (2.12) are divergent. We can circumvent this difficulty by subtracting from (2.12) the corresponding expressions for free space:

$$U_k^0 = -\alpha_k \mathrm{Tr}\, \underline{\underline{\mathcal{D}}}^0(\underline{R}_k, \underline{R}_k) \,, \quad k = 1,2 \tag{2.14}$$

where $\underline{\underline{\mathcal{D}}}^0(\underline{R},\underline{R}')$ is the free space dyadic Green's function. After that the renormalized single molecule energies can be obtained from the densities:

$$U_k = \alpha_k \mathrm{Tr}\, \underline{\underline{\mathcal{D}}}_B^1(\underline{R}_k, \underline{R}_k) \,, \quad k = 1,2 \tag{2.15}$$

where $\underline{\underline{\mathcal{D}}}_B^1(\underline{R},\underline{R}')$ is the reflected (or scattered, or induced) dyadic Green's function due to B:

$$\underline{\underline{\mathcal{D}}}_B^1(\underline{R},\underline{R}') = \underline{\underline{\mathcal{D}}}_B(\underline{R},\underline{R}') - \underline{\underline{\mathcal{D}}}^0(\underline{R},\underline{R}') \,. \tag{2.16}$$

The concept of the reflected Green's function is also helpful in separating the terms describing the effect of the substrate on the mutual interaction between the molecules. Expressing $\underline{\underline{\mathcal{D}}}_B$ as the sum of $\underline{\underline{\mathcal{D}}}^1_B$ and $\underline{\underline{\mathcal{D}}}^0$ from (2.13) we obtain:

$$U_{12} = -\alpha_1\alpha_2 \mathrm{Tr}\{\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_1,\underline{R}_2)\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_2,\underline{R}_1) + \underline{\underline{\mathcal{D}}}^0(\underline{R}_1,\underline{R}_2)\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_2,\underline{R}_1) + \underline{\underline{\mathcal{D}}}^0(\underline{R}_2,\underline{R}_1)\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_1,\underline{R}_2)\} - \alpha_1\alpha_2 \mathrm{Tr}[\underline{\underline{\mathcal{D}}}^0(\underline{R}_1,\underline{R}_2)\underline{\underline{\mathcal{D}}}^0(\underline{R}_2,\underline{R}_1)] \quad . \tag{2.17}$$

Now it becomes obvious that the last term in eq (2.17) describes the interaction between the molecules in free space, whilst the first term represents the correction to this interaction due to the body B.

2.3 Van der Waals interaction between molecules near a dielectric halfspace.

As we have mentioned this problem has first been solved by McLachlan [2] and a generalization of it by Richmond and Sarkies [3]. Nonetheless, since we shall need the intermolecular potential between adsorbed molecules at a gas-solid interface, and to illustrate the general formalism by an example we give an analysis of it below.

The geometry of the system is shown in Fig. 2.1. We limit ourselves to the nonretarded approximation, hence we assume that the reflected dyadic Green's function can be obtained from the potential of the image charge [8]:

$$\phi^1_B(\underline{R}_1,\underline{R}_2) = \frac{-1}{[(\underline{r}_1-\underline{r}_2)^2+(z_1+z_2)^2]^{\frac{1}{2}}} \cdot \frac{\varepsilon-1}{\varepsilon+1} \tag{2.18}$$

where ε is the dielectric permittivity of the body B; $\underline{r}_1,\underline{r}_2$ are the projections of $\underline{R}_1,\underline{R}_2$ onto the xy plane (which coincides with the surface of B); and z_1,z_2 are the Z-components of the position vectors $\underline{R}_1$ and

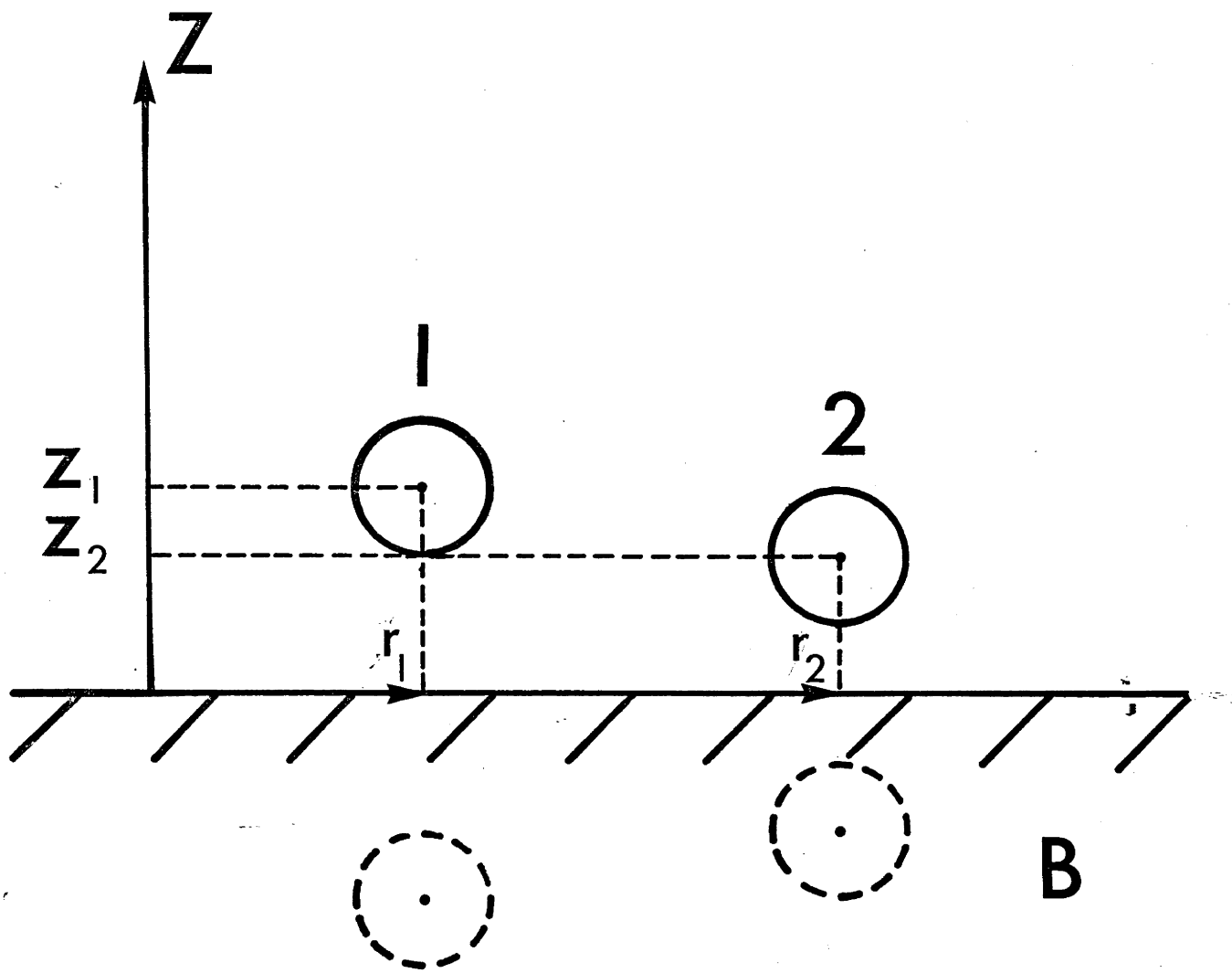

Fig. 2.1. The molecules above the dielectric B. The broken line displays the mirror images inside B.

$\underline{R}_2$. The relation between the reflected dyadic Green's function and the image potential is:

$$\underline{\underline{\mathcal{D}}}_B^1(\underline{R}_1,\underline{R}_2) = \nabla_{\underline{R}_1}\nabla_{\underline{R}_2}\,\phi_B^1(\underline{R}_1,\underline{R}_2) \quad . \tag{2.19}$$

In the nonretarded approximation the free space dyadic has the form:

$$\underline{\underline{\mathcal{D}}}^0(\underline{R}_1,\underline{R}_2) = \nabla_{\underline{R}_1}\nabla_{\underline{R}_2}\,\frac{1}{|\underline{R}_1 - \underline{R}_2|} \quad . \tag{2.20}$$

Upon substituting eqs (2.20) and (2.19) into (2.17) and performing some algebra we obtain:

$$U_{12} = \alpha_1\alpha_2 \left\{ \frac{2}{(R_{im}R)^3} \left[1 + \frac{9}{(R_{im}R)^2} (r^2-(z_1^2-z_2^2))^2 + \frac{3}{R^2} ((z_1-z_2)^2-r^2) \right.\right.$$
$$\left.\left. + \frac{3}{R_{im}^2} ((z_1+z_2)^2-r^2) \right] \frac{\varepsilon-1}{\varepsilon+1} - \frac{6}{R_{im}^6} \left(\frac{\varepsilon-1}{\varepsilon+1}\right)^2 \right\} - \frac{6\alpha_1\alpha_2}{R^6} \qquad (2.21)$$

where: $r = |\underline{r}_1-\underline{r}_2|$, $R_{im} = (r^2+(z_1+z_2)^2)^{\frac{1}{2}}$, $R = (r^2+(z_1-z_2)^2)^{\frac{1}{2}}$.
When $z_1 = z_2 = z$, i.e. the molecules are at the same height above the surface, the last equation can be simplified to:

$$U_{12} = \alpha_1\alpha_2 \left\{ \frac{8}{(r^2+4z^2)^{3/2} r^3} \left[1 - \frac{3z^2}{r^2+4z^2} \right] \frac{\varepsilon-1}{\varepsilon+1} \right.$$
$$\left. - \frac{6}{(r^2+4z^2)^3} \left(\frac{\varepsilon-1}{\varepsilon+1}\right)^2 \right\} - \frac{6\alpha_1\alpha_2}{r^6} \quad . \qquad (2.22)$$

We can estimate the upper limit of the substrate effect on the interactions between the molecules by letting $\varepsilon \to \infty$ in the above expression. Then the ratio of the first term to the other of eq (2.22) follows as:

$$\left| \frac{\Delta F_{12}^B}{F_{12}^0} \right| \equiv \left| \frac{\Delta U_{12}^B}{U_{12}^0} \right| = \frac{4}{3} \frac{r^3}{(r^2+4z^2)^{3/2}} \left[1 - \frac{3z^2}{r^2+4z^2} \right] - \frac{r^6}{(r^2+4z^2)^3} \qquad (2.23)$$

where F_{12}^0 is the interaction free energy in the absence of B and ΔF_{12}^B is the contribution due to the substrate. For $r >> z$ the value of this ratio is 1/3. In the next chapter we shall discuss the contribution of the substrate to the intermolecular interactions for other dielectric permittivities, so that we just mention here that this contribution does not depend significantly on ε; therefore the value of 1/3 is a good estimate in general.

In concluding this section we write the van der Waals interaction potential between the molecules and the single molecule adsorption energy using the zero-temperature approximation. In the limit $T \to 0$ the sum over the frequencies $\xi_n = 2\pi nkT/\hbar$ can be replaced by the integral:

$$\lim_{T\to 0} kT \sum_{n=0}^{\infty} f(i\xi_n) = \frac{\hbar}{2\pi} \int_0^{\infty} f(i\xi) d\xi \tag{2.24}$$

where $f(i\xi)$ is an arbitrary function. In this limit, the free energies of interaction become equal to the internal energies and from (2.9), (2.15) and (2.24) we can write:

$$\lim_{T\to 0} F_\ell(z_\ell) = E_\ell(z_\ell) = -\frac{\hbar}{4\pi z_\ell^3} \int_0^{\infty} \alpha_\ell(i\xi)\Delta(i\xi) d\xi \tag{2.25}$$

where $\Delta(i\xi) = \dfrac{\varepsilon(i\xi)-1}{\varepsilon(i\xi)+1}$.

Similarly for $F_{12}(\underline{R}_1, \underline{R}_2)$ we obtain (we limit ourselves to the case $z_1 = z_2 = z$):

$$\begin{aligned}
\lim_{T\to 0} F_{12}(\underline{R}_1, \underline{R}_2) \equiv V_{12}(|\underline{r}_1 - \underline{r}_2|, z_1 = z_2 = z) = \\
= \frac{\hbar}{2\pi} \frac{8}{(r^2+4z^2)^{3/2} r^3} \left(1 - \frac{3z^2}{r^2+4z^2}\right) \int_0^{\infty} \alpha_1(i\xi)\alpha_2(i\xi)\Delta(i\xi) d\xi \\
- \frac{\hbar}{2\pi} \frac{6}{(r^2+4z^2)^3} \int_0^{\infty} \alpha_1(i\xi)\alpha_2(i\xi) [\Delta(i\xi)]^2 d\xi \\
+ \frac{\hbar}{2\pi} \frac{6}{r^6} \int_0^{\infty} \alpha_1(i\xi)\alpha_2(i\xi) d\xi
\end{aligned} \tag{2.26}$$

where $r = |\underline{r}_1 - \underline{r}_2|$.

2.4 Effect of spatial dispersion on van der Waals interaction between molecules.

THE NON-LOCAL relation between the macroscopic electric field $\underline{E}$ and the dielectric displacement $\underline{D}$ in a spatially dispersive medium introduces complications in the theory of van der Waals (vdW) interactions between molecules in and near such media. Even for the simplest geometries, e.g. interactions in a layer of uniform electrolyte solution [9], or between two metal plates [10,11], the calculations become so involved that physical intuition is obscured. This is mainly due to pragmatic difficulties associated with the solution of Maxwell's equations with non-local (integral) relations which connect $\underline{D}$ (not to be confused with the dyadic Green's function) and $\underline{E}$. In many practical applications one has to deal with much more complicated structures as, for example, pores in adsorption problems. In seeking some insight into the general question - when can one neglect the effect of a non-local dielectric response on vdW interactions? - it seems reasonable to explore first the simplest possible situations. We analyse the problem here for the case of interactions between two molecules which are (a) embedded in a homogeneous medium and (b) adsorbed at the vacuum-metal interface. We assume that the hydrodynamic dielectric function [12] gives an appropriate description of the medium, and comment on that approximation below. The adsorption of a single molecule on a metal surface has been considered by several authors [13,14] . We recover their results and additionally establish criteria for deciding when the influence of spatial dispersion of the metal on the heat of adsorption can be neglected.

2.4.1 Molecules in a homogeneous electron gas

Assume that two molecules are embedded in an infinite homogeneous medium described by a dielectric function

$$\varepsilon(\underline{q},\omega) = 1 + \frac{\omega_p^2}{\underline{q}^2\beta^2 - i\gamma\omega - \omega^2} \tag{2.27}$$

where $\underline{q}$ is the three-dimensional wave number vector. The above expression for the dielectric function is obtained from the hydrodynamic model for the electron gas in metals. In general, any dielectric function $\varepsilon(\underline{q},\omega)$ arises out of the non local relationship between the vectors $\underline{D}$ and $\underline{E}$ in a homogeneous medium:

$$\underline{D}(\underline{R},t) = \int_{-\infty}^{t} dt' \int d^3\underline{R}\,\varepsilon(\underline{R}-\underline{R}',t-t')\underline{E}(\underline{R}',t') \; . \tag{2.28}$$

Indeed, applying the space-time Fourier transform to (2.28) we obtain:

$$\underline{D}(\underline{q},\omega) = \varepsilon(\underline{q},\omega)\underline{E}(\underline{q},\omega) \tag{2.29}$$

where:

$$\varepsilon(\underline{q},\omega) = \int_{-\infty}^{+\infty} \theta(t)dt \int d^3\underline{R}\; e^{-i(\underline{q}\cdot\underline{R}-\omega t)}\varepsilon(\underline{R},t) \quad . \tag{2.30}$$

The measure of the spatial dispersion in the hydrodynamic model (eq (2.27)) is the phenomenological parameter β which is related to the Fermi velocity in metals $\beta^2 = 0.6\ V_F^2$ [15]. Other parameters in eq (2.27) are: ω_p - the plasma frequency, which is related to the density number, mass and charge of electrons as

$$\omega_p^2 = 4\pi Ne^2/m, \tag{2.31}$$

and γ, the typical half-width of the absorption band near the frequency ω_p.

We restrict analysis to the nonretarded approximation so that the space-time Fourier transform of the potential of an oscillating

monopole at $\underline{R} = 0$ is:

$$\Phi(\underline{q},\omega) = \frac{1}{\varepsilon(\underline{q},\omega)q^2} \quad . \tag{2.32}$$

Eq (2.32) is readily obtained from Poisson's equation. We point out here that an important omission of the hydrodynamic model is the singularity in $\varepsilon(\underline{q},\omega=0)$ which leads to the long-range Friedel oscillations in $\Phi(\underline{R},0)$ [16]. Thus only qualitative conclusions are possible with regard to metals. In a realistic model for $\varepsilon(\underline{q},\omega)$ one has effects due to Friedel oscillations [16], although the magnitude of such long-range terms is found to be much smaller than that for the interactions discussed here.

Bearing in mind all these limitations we proceed. From eqs (2.32) and (2.27) the inverse Fourier transform follows as

$$\Phi(\underline{R},\omega) = \left(\frac{\omega^2+i\gamma\omega}{\omega_p^2-i\gamma\omega-\omega^2}\right)\frac{1}{R} + \frac{e^{-\lambda R}}{R}\left(1 - \frac{\omega^2+i\gamma\omega}{\omega_p^2-i\gamma\omega-\omega^2}\right) \tag{2.33}$$

where $\lambda^2 = \dfrac{(\omega_p^2-i\gamma\omega-\omega^2)}{\beta^2}$.

For the van der Waals interactions we can let $\gamma=0$, since the effect of damping is known to be very small [17].

Calculating the dyadic Green's function:

$$\underline{\underline{\mathcal{D}}}(\underline{R}_i,\underline{R}_j,\omega) = \nabla_{\underline{R}_i}\nabla_{\underline{R}_j}\Phi(\underline{R}_i-\underline{R}_j,\omega), \quad j = 1,2 \tag{2.34}$$

and substituting into eq (2.13) we obtain after some algebra:

$$\begin{aligned} U_{12} = -\alpha_1\alpha_2\Bigg\{ & \frac{6h^2}{R^6} + 2h(1-h)e^{-\lambda R}\left(\frac{3}{R^6} + \frac{6\lambda}{R^5} + \frac{2\lambda^2}{R^4}\right) \\ & + (1-h)^2 e^{-2\lambda R}\left(\frac{6}{R^6} + \frac{12\lambda}{R^5} + \frac{5\lambda^2}{R^4} + \frac{4\lambda^3}{R^3} + \frac{\lambda^4}{R^2}\right)\Bigg\} \end{aligned} \tag{2.35}$$

where $h \equiv h(i\xi) = \frac{\xi^2}{\omega_p^2+\xi^2}$ and $\lambda \equiv \lambda(i\xi) = \frac{(\omega_p^2+\xi^2)^{\frac{1}{2}}}{\beta}$.

It is convenient to introduce short-range and long-range parts of the interaction energy density (2.35) as:

$$U_{12}(SR) = -\alpha_1\alpha_2 \left\{2h(1-h)e^{-\lambda R}\left(\frac{3}{R^6} + \frac{6\lambda}{R^5} + \frac{2\lambda^2}{R^4}\right) + \right.$$

$$\left. + (1-h)^2 e^{-2\lambda R}\left(\frac{6}{R^6} + \frac{12\lambda}{R^5} + \frac{5\lambda^2}{R^4} + \frac{4\lambda^3}{R^3} + \frac{\lambda^4}{R^2}\right)\right\} \tag{2.36a}$$

$$U_{12}(LR) = -\alpha_1\alpha_2 \frac{6h^2}{R^6} . \tag{2.36b}$$

The interaction energies of short- and long-range can be calculated according to:

$$E_{12}(SR) = \frac{\hbar}{2\pi}\int_0^\infty U_{12}(SR,i\xi)d\xi \tag{2.37a}$$

$$E_{12}(LR) = \frac{\hbar}{2\pi}\int_0^\infty U_{12}(LR,i\xi)d\xi . \tag{2.37b}$$

It is easy to calculate the long-range part $E_{12}(LR)$ exactly, using for the polarizabilities of the molecules eq (2.1), where, for simplicity, we put $\omega_{01} = \omega_{02} = \omega_0$. Carrying out the integration in (2.37b) we obtain:

$$E_{12}(LR) \equiv \frac{\hbar}{2\pi}\int_0^\infty \frac{6\alpha^2(i\xi)h^2(i\xi)}{R^6} = \frac{C}{R^6}\alpha_0^2 \tag{2.38}$$

where

$$C = 3\hbar\omega_0^4\left\{\frac{1}{4\omega_0^3} - \frac{\omega_p^2}{\omega_0^2-\omega_p^2}\left(\frac{1}{\omega_0\omega_p(\omega_0+\omega_p)} - \frac{1}{2\omega_0^3}\right)\right.$$

$$\left. + \frac{\omega_p^4}{(\omega_0^2-\omega_p^2)^2}\left[\frac{1}{4}\left(\frac{1}{\omega_p^3}+\frac{1}{\omega_0^3}\right) - \frac{1}{\omega_0\omega_p(\omega_0+\omega_p)}\right]\right\} . \tag{2.39}$$

The short-range part, $E_{12}(SR)$, is more involved and is best evaluated

numerically. We have computed the ratio $E_{12}(SR)/E_{12}$ for various R taking as values of the parameters (in the system of units where $e = \hbar = m = 1$):

$\omega_p = 0.565$ atomic units (a.u.), $\beta = 0.77$ a.u. and $\omega_0 = 0.7$ a.u.

These values of ω_p and β are appropriate to aluminium and ω_0 is a typical ultraviolet frequency. The ratio $E_{12}(SR)/E_{12}$ is plotted in Fig. 2.2, and it can be seen that for distances greater than 7 a.u. (≈ 3.5 Å) the short-range part accounts for less than 10% of the total energy of interaction.

2.4.2 Molecules near a metallic halfspace

Now assume that the molecules occupy positions $\underline{R}_1 = (\underline{r}_1, z_1)$ and $\underline{R}_2 = (\underline{r}_2, z_2)$ where $z_1, z_2 > 0$ above a metallic semi-infinite medium extending through the region $z < 0$ (cf. Fig. 2.1). The region $z > 0$ is a vacuum. We need to find the reflected dyadic Green's function $\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_1, \underline{R}_2)$, which in the nonretarded approximation can be obtained from the induced potential $\phi^1(\underline{R}_1, \underline{R}_2)$ due to an oscillating monopole at $\underline{R}_2$. This potential is of interest in solid-state theory so that several authors have tackled the problem of finding it [18-20]. Here we shall adopt the results of Beck and Celli [21]. These authors derived the induced potential on the assumptions of an infinite potential barrier at the vacuum-metal interface, so that specular reflection of electrons takes place at this interface. As far as physical adsorption problems are concerned that model is valid since the energies involved are much smaller than the work function of the metals. (By definition, physical adsorption occurs when the adsorbed molecule does not form a chemical bond with the substrate so that the electrons in the molecule are distinguishable from those of the metal.)

Following, therefore, Beck and Celli [21] we can write the expression for the induced potential as:

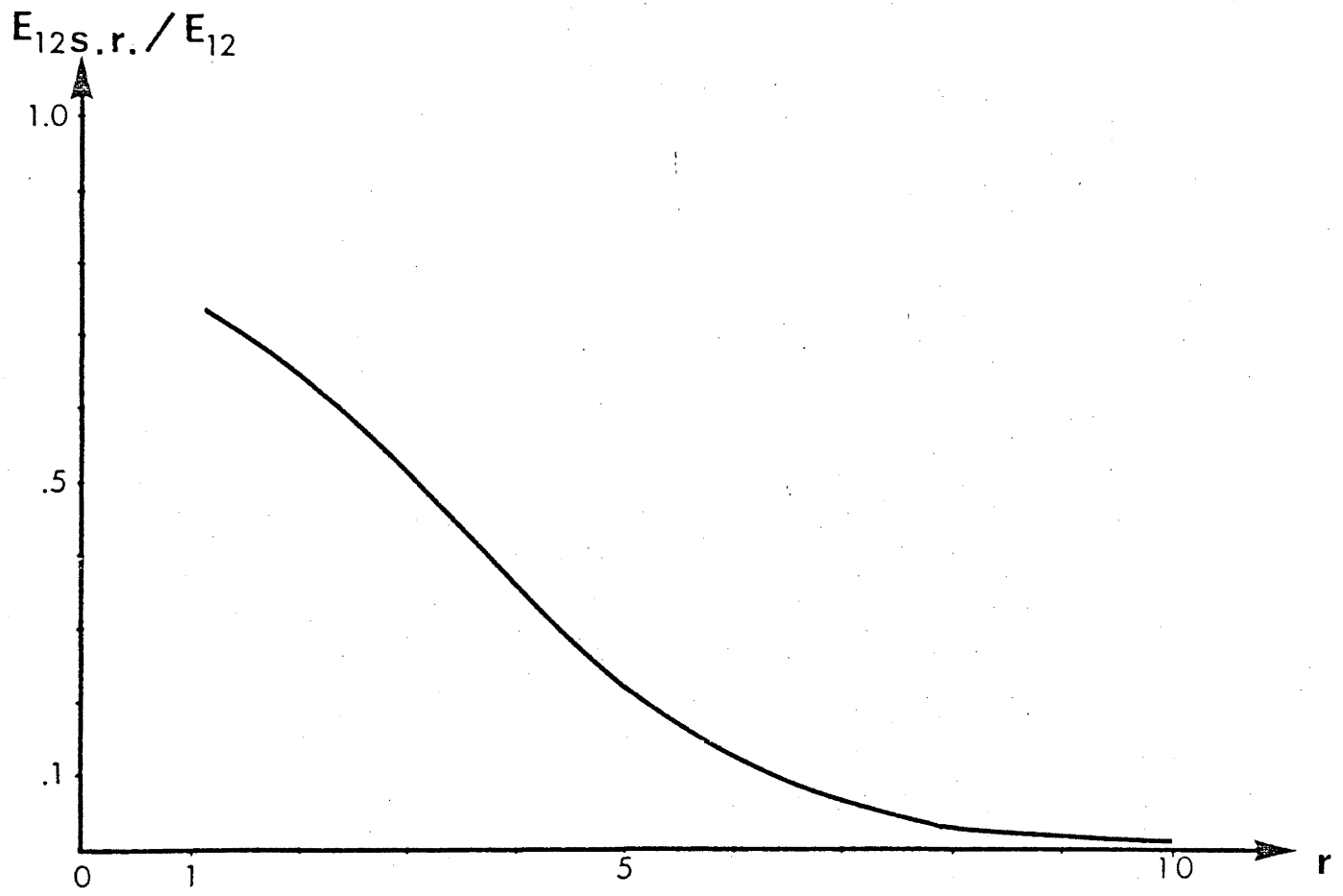

Fig. 2.2. The short-range part (due to the spatial dispersion) to the total vdW energy between the molecules in a homogeneous medium (data appropriate for Al). The distances are in atomic units.

$$\phi^1(\underline{R}_1,\underline{R}_2) = -\frac{1}{2\pi}\int d^2k\,\frac{e^{-k(z_1+z_2)}}{k}\,S(k)e^{-\underline{k}\cdot\underline{r}} \tag{2.40}$$

where $\underline{r} = \underline{r}_1-\underline{r}_2$ and $S(k)$ is a function which does not depend on the external charge and can be evaluated from the bulk dielectric function $\varepsilon(\underline{q},\omega)$ through an integral equation. In eq (2.40) the vector $\underline{k}$ is the XY-plane projection of the three-dimensional vector $\underline{q}$ so that $\underline{q} = (\underline{k},q_z)$

The form of equation (2.40) lends itself to asymptotic expansion for large z_1+z_2. Assuming that $S(k)$ is a well-behaved function of k we can convert (2.40) to cylindrical coordinates and integrate by parts with respect to k N-times. This yields:

$$\phi^1(\underline{R}_1,\underline{R}_2) = -\frac{1}{2\pi}\sum_{n=0}^{N}\int_0^{2\pi} d\psi\,\frac{S^{(n)}(0)}{(z_1+z_2+ir\cos\psi)^{n+1}} \tag{2.41}$$

$$-\frac{1}{2\pi}\int_0^{2\pi} d\psi\int_0^{\infty} dk\,S^{(N+1)}(k)\,\frac{e^{-ikr\cos\psi-k(z_1+z_2)}}{(z_1+z_2+ir\cos\psi)^{N+1}}\,.$$

Denote the first term of eq (2.41) by $\phi_N^1(\underline{R}_1,\underline{R}_2)$, the other by $H_N(\underline{R}_1,\underline{R}_2)$ and define $z' = z_1+z_2$, $R' = (r^2+z'^2)^{\frac{1}{2}}$. Then we can express ϕ_N^1 as

$$\phi_N^1(\underline{R}_1,\underline{R}_2) = -\sum_{n=0}^{\infty}(-1)^n\,\frac{S^{(n)}(0)}{n!}\,\frac{\partial}{\partial z'^n}\,\frac{1}{R'}\,. \tag{2.42}$$

The difference between the approximate and exact potential can be estimated as:

$$\left|\phi^1(\underline{R}_1,\underline{R}_2) - \phi_N^1(\underline{R}_1,\underline{R}_2)\right| \equiv \left|H_N(\underline{R}_1,\underline{R}_2)\right| \leqslant \frac{A_N}{(z_1+z_2)^{N+2}} \tag{2.43}$$

where A_N is the maximum value of the derivative $S^{(N+1)}(k)$ for all $k \geqslant 0$.

From the asymptotic form of the induced potential (2.42) follows an asymptotic expression for the dyadic Green's function $\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_1,\underline{R}_2)$ since

$$\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_1,\underline{R}_2) = \nabla_{\underline{R}_1}\nabla_{\underline{R}_2}\phi^1_N(\underline{R}_1,\underline{R}_2) + \nabla_{\underline{R}_1}\nabla_{\underline{R}_2}H_N(\underline{R}_1,\underline{R}_2) \quad . \tag{2.44}$$

Performing simple, though tedious, calculations we arrive at the following asymptotic forms of the energy densities $U_{12}(i\xi)$ and $U_j(i\xi)$, $j = 1,2$:

$$U_j(\underline{R}_j,i\xi) = -4 \sum_{n=0}^{N} S^{(n)}(0,i\xi) \frac{1}{(2z_j)^{n+3}} \quad , \quad j = 1,2 \tag{2.45}$$

and

$$U_{12}(\underline{R}_1,\underline{R}_2,i\xi) = -\alpha_1\alpha_2 \left\{ \frac{6}{R^6} - \frac{4}{R^3}\left[2\frac{\partial^2 g_N}{\partial z'^2} + \frac{3r^2}{R^2}\frac{\partial^2 g_N}{\partial r^2}\right] + \right.$$

$$\left. + 8\left[\left(\frac{\partial^2 g_N}{\partial z'^2}\right)^2 + \left(\frac{\partial^2 g_N}{\partial z'^2}\right)^2 + \left(\frac{\partial^2 g_N}{\partial r \partial z'}\right)^2 + \left(\frac{\partial^2 g_N}{\partial r^2}\right)\left(\frac{\partial^2 g_N}{\partial z'^2}\right)\right]\right\} \tag{2.46}$$

where $R = |\underline{R}_1 - \underline{R}_2|$ and g_N is given by:

$$g_N(\underline{R}_1,\underline{R}_2,i\xi) = \sum_{n=0}^{N} \frac{(-1)^n}{(n+2)!} S^{(n)}(0,i\xi) \frac{\partial^n}{\partial z'^n}\frac{1}{R'} \quad . \tag{2.47}$$

For $N=0$ we arrive at eq (2.21) provided we identify $S(0)$ with $\Delta = \frac{\varepsilon-1}{\varepsilon+1}$.

So far the function $S(k,\omega)$ has been taken as arbitrary and depends only on the choice of the model for the metal. We specialize now to the quasiclassical approximation for $S(k,\omega)$ [21]

$$S(k,\omega) = \frac{\varepsilon'(k,\omega)-1}{\varepsilon'(k,\omega)+1} \tag{2.48}$$

where

$$[\varepsilon'(k\omega)]^{-1} = \frac{k}{\pi}\int_{-\infty}^{+\infty}\frac{dq_z}{q\varepsilon(\underline{q},\omega)} \tag{2.49}$$

(with $\underline{q} = (\underline{k},q_z)$). The same form of $S(k,\omega)$ has been arrived at by Chan and Richmond by a different method [13]. If the hydrodynamic approximation to $\varepsilon(\underline{q},\omega)$ holds (eq (2.27)) then from eqs (2.48) and (2.49) we have:

$$S(k,i\xi) = \frac{(\xi^2+\gamma\xi+\omega_p^2+\beta^2k^2)^{\frac{1}{2}}-\beta k}{(1+2(\xi^2+\gamma\xi)/\omega_p^2)(\xi^2+\gamma\xi+\omega_p^2+\beta^2k^2)^{\frac{1}{2}}+\beta k} \quad . \tag{2.50}$$

As we have mentioned earlier, we can neglect the damping factor γ as long as the dispersion interactions are concerned. By direct differentiation with respect to k we can find any derivative $S^{(n)}(k,i\xi)$ which is required to calculate the energy densities through eq (2.45)-(2.47). To find the error made by truncating the expansions (2.40), (2.45) and (2.47) at zeroth, first or second order terms, we can use the estimates (with $\gamma=0$)

$$A_1^0 \leqslant \frac{2(\xi^2+\omega_p^2)^{\frac{1}{2}}\beta}{\omega_p^2(1+2\xi^2/\omega_p^2)^2}, \qquad A_2^1 \leqslant \frac{5.72}{(1+2\xi^2/\omega_p^2)^2}\cdot\frac{\beta^2}{\omega_p^2}$$

$$A_3 \leqslant \frac{24}{(1+2\xi^2/\omega_p^2)^2(1+\xi^2/\omega_p^2)^{\frac{1}{2}}}\cdot\frac{\beta^3}{\omega_p^3} \quad . \tag{2.51}$$

In particular with values of β and ω_p for Al, the error made in approximating E_1 by the zeroth order term (or taking $\beta=0$) is less than 12% for $z_1, z_2 >$ a.u.

To see the effect of spatial dispersion on adsorption energies we have computed the energies $E_1(\beta,z)$, $E_1(0,2)$, $E_{12}(\beta,r)$ and $E_{12}(0,r)$ using the low temperature approximation. In Fig. 2.3 we plot the ratio $E_1(\beta,z)/E_1(0,z)$ and in Fig. 2.4 the functions $p(r)$ and $q(1)$

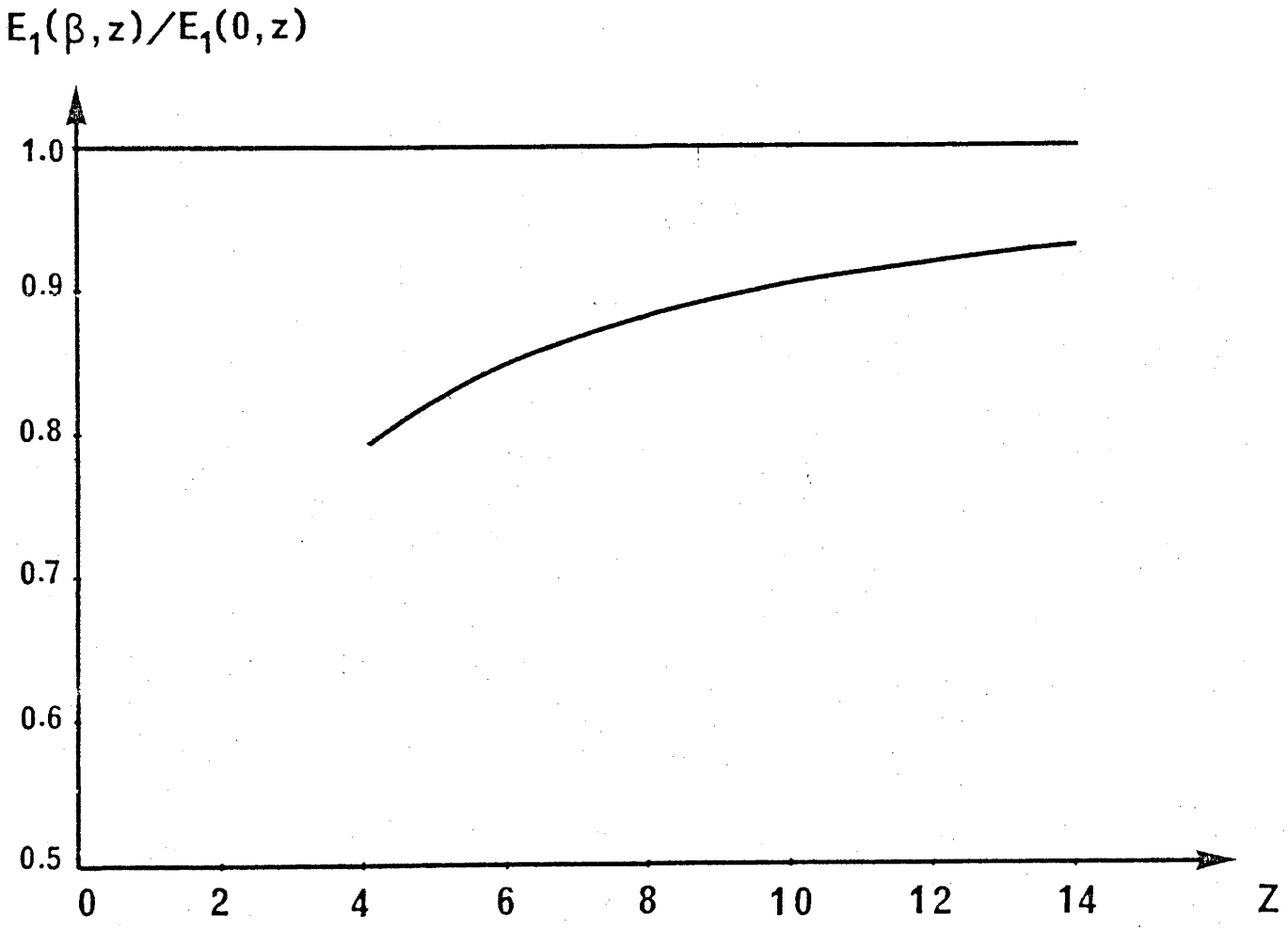

Fig. 2.3. The adsorption energy calculated accounting for the spatial dispersion - $E_1(\beta,z)$ to that calculated by using the local dielectric function ($\beta=0$) $-E_1(0,z)$. The data are appropriate for Al and the distances are in atomic units.

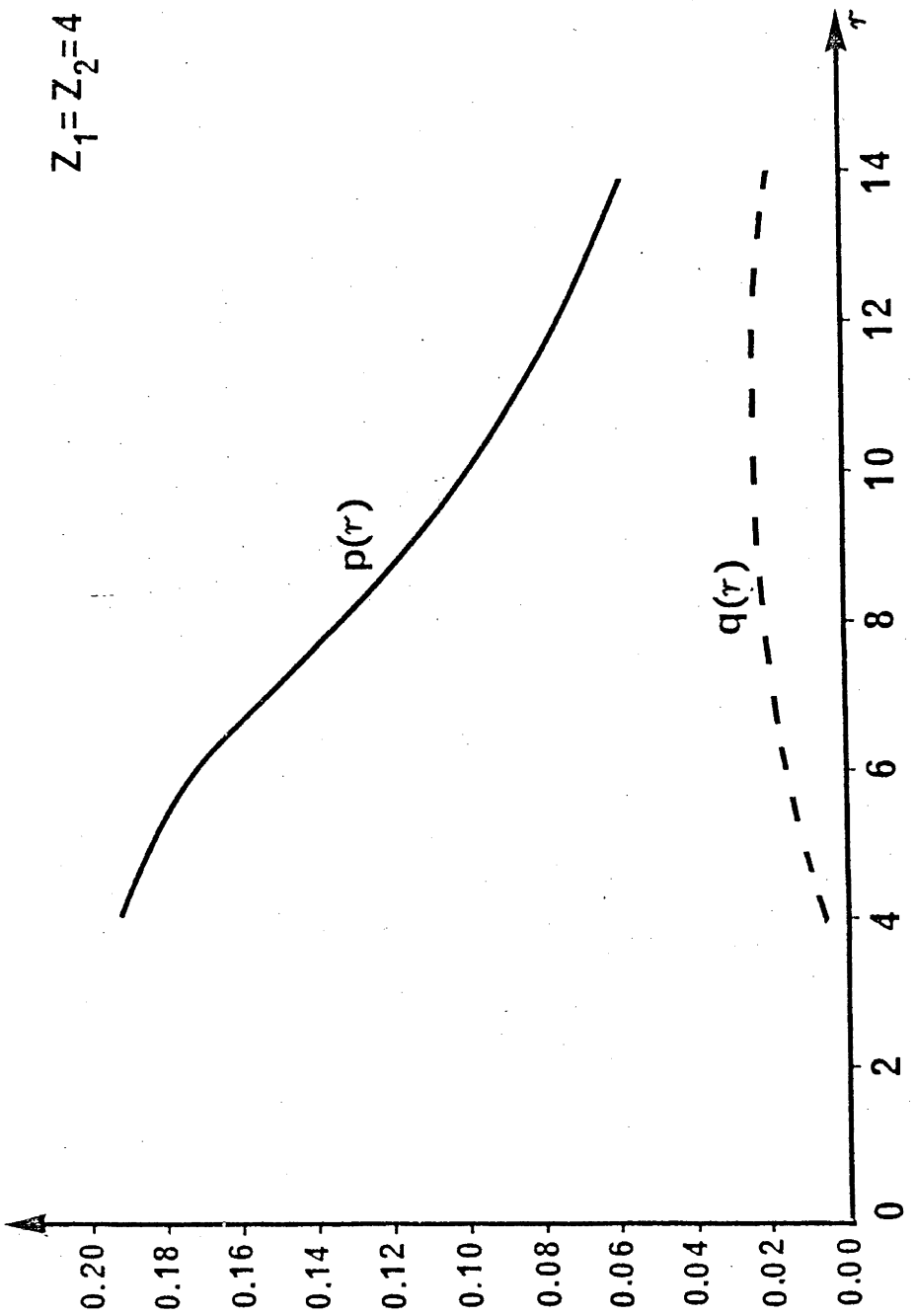

Fig. 2.4. For the definition of p(r) and q(r) see text.

defined as

$$p(r) = \frac{|E_{12}(\beta,r) - E_{12}(0,r)|}{|E_{12}(0,r) - E_{12}^{0}(0,r)|} \tag{2.52}$$

and

$$q(r) = |E_{12}(\beta,r) - E_{12}(0,r)|/|E_{12}(r)| \tag{2.53}$$

where $E_{12}^{(0)}(r) = \lim_{z\to\infty} E_{12}(r)$, i.e. the energy of interaction in free space. In plotting these curves, it was assumed that $z_1 = z_2 = 4$ a.u. and $T = 100$ K. From Figs. 2.2-2.4 two conclusions can be drawn. First the energy of interaction between the molecules E_{12} is affected by spatial dispersion only for very small distances of the order of a few atomic units. Thus in practical applications we need not bother with non-local properties of the medium so long as we do not consider the chemical binding between atoms or molecules when the distances are of this order. Secondly, spatial dispersion has some effect on the adsorption energy at zero coverage when the approximation $\beta = 0$ gives an error of about 12% at a distance (typical for physisorption) between molecule and substrate of about 10 a.u. However, as the distance between the molecule and the surface increases the error in neglecting spatial dispersion descreases at a rate $\propto$ 1/distance. The inequality (2.43) can be used as a rough criterion for what distances we can use a local dielectric description of the metal.

It should be emphasised again that the above results are only qualitative as we have assumed a hydrodynamic model for the dielectric function of the bulk metal. Nonetheless the present discussion should provide some confidence for the validity of those applications based on a local dielectric description when the distances between molecule-molecule or molecule-substrate are not too small.

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CHAPTER 3

DISPERSION FORCES IN PHYSICAL ADSORPTION

3.1 Preamble

The attractive force between molecules and surfaces of solids or liquids is responsible for the whole range of phenomena collectively termed adsorption. In physical adsorption the internal states of the adsorbed molecules (adsorbates) and the atoms on the attracting surface (adsorbent) are not strongly perturbed, so that the force between them is of dispersion (and possibly electrostatic) nature. In view of this it is not surprising that physical adsorption experiments can, and do, provide verifications of the van der Waals forces theory.

Theoretical descriptions of the adsorption process date back to Gibbs [1,2] who was the first to establish a formal thermodynamic relation between adsorbed films and bulk parameters. Subsequent work by Fowler and Guggenheim [3], Hill [4] and de Boer [5] brought the statistical thermodynamics of adsorption to the form which is mostly used by present-day workers in this field. There exist, however, new trends in the adsorption theories where "hard-core" statistical mechanics is employed; to mention more recent works by Mitchell and Richmond [6], Richmond [7], Perram and Smith [8] and Henderson, Abraham and Barker [9]. We confine ourselves to a simple picture of the adsorbed monolayer as an imperfect two-dimensional (2-D) gas [5], whose parameters are related to those of the bulk gas through an adsorption isotherm equation. There is strong experimental evidence that whenever one has to do with a homogeneous smooth substrate the behaviour of the adsorbed monolayer resembles very much the behaviour of bulk imperfect gases [2,10].

Of all semi-empirical models for imperfect gases the best known is the van der Waals gas model. Its 2-D version has been introduced to the physical adsorption by Hill [4] and later de Boer [5]. The corresponding Hill-de Boer adsorption isotherm has been shown to be particularly suitable in describing monolayer adsorption of inert gases on graphitized carbon black [11]. This isotherm relates the 3-D bulk gas pressure to the degree of coverage of the adsorbent surface, θ (defined as the surface density σ to the maximum density when the monolayer is close packed-σ_0), and has the following form

$$p = k_1 \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - k_2\theta\right). \tag{3.1}$$

The coefficients k_1 and k_2 are usually fitted from experiments, although one may relate k_2 to the 2-D van der Waals coefficients a_2 and b_2: $k_2 = 2a_2/b_2$ [5] (cf. the next section).

When the value of the van der Waals coefficients a_2 and b_2 is calculated with aid of the intermolecular potential of the same form as in bulk gas, one obtains values of the critical temperature for 2-D condensation about 20% higher than the experimental ones. In the next section we provide an explanation of this discrepancy in the light of substrate mediated interactions between adsorbate molecules (cf. also [12]).

Section 3.3 touches upon the important question of the influence of surface topography on adsorption energies. It has long been recognized that the adsorbent-adsorbate potential is increased in pores of molecular dimensions (see, for example, the review by K.S.W. Sing [13]). The theoretical calculations have been made on the basis of pairwise summation of the molecular potential between adsorbate and adsorbent molecules (even for planar substrates) [14-17]. We propose here

to use the formalism of dispersion forces and consider as examples the adsorption energy in the corner of a step on a metal substrate and estimate the adsorption potential near the middle of a cross-section of a very long micropore.

The Chapter ends with comments on the measurements of van der Waals forces between heavy alkali atoms and gold surfaces. These experiments were carried out recently by Shih and Parsegian [18]. We suggest that the dielectric properties of an aggregated gold film are responsible for the fact that the experimental values of the van der Waals potentials between Cs, Rb and W, and gold surfaces are smaller than the predictions based on the dielectric permittivity values appropriate to the bulk gold.

3.2 Two-dimensional van der Waals gas

In an ingenious way van der Waals derived in 1873 the gas equation of state which accounts for both the long-range attractive molecular forces and short-range repulsion between the constituent molecules. The first effect influences the observed pressure p that gas exerts on the walls of a container, whilst the second makes the available volume somewhat smaller compared with the corresponding volume for an ideal gas, V. When these corrections are introduced to the ideal gas equation of state, one obtains:

$$\left(p + a_3 \frac{N^2}{V^2}\right) (V - Nb_3) = NkT \tag{3.2}$$

where N is the number of molecules and a_3, b_3 are constants assumed to be independent on N, V and T. We have introduced here the subscript 3 to emphasize that eq (3.2) refers to the bulk gas.

The argument used by van der Waals carried through to a mobile monolayer adsorbed on a plane smooth substrate. In this case one has the spreading pressure, π, instead of p, and the surface area, A, in place of V. Now the 2-D analogue of eq (3.2) assumes the form:

$$\left(\pi + a_2 \frac{N^2}{A^2}\right) (A - Nb_2) = NkT . \tag{3.3}$$

The 2-D isotherms plotted on the π-A diagram are similar to their 3-D counterparts and one can easily interpret the 2-D phase transitions, and establish the 2-D critical parameters. These are [5]:

$$\text{a)} \quad \pi_c = \frac{a_2}{27b_2^2}, \qquad \text{b)} \quad T_c = \frac{1}{k}\frac{8a_2}{27b_2}, \qquad \text{c)} \quad \sigma_c = \frac{b_2}{3} \tag{3.4}$$

that is, formally identical with the 3-D critical parameter. Later we shall use the critical temperature ratio: $T_c(2\text{-D})/T_c(3\text{-D})$ which turns out to be

$$T_c(2\text{-D})/T_c(3\text{-D}) = \frac{a_2}{a_3} \cdot \frac{b_3}{b_2} . \tag{3.5}$$

In the adsorption literature one finds in common use the virial expansion of the 2-D equation of state [3]:

$$\pi = \sigma kT(1+\sigma B_2+\sigma^2 B_3+ \ldots.), \quad \sigma = \frac{N}{A} \tag{3.6}$$

where the coefficients B_2, B_3, etc. are determined from statistical considerations. In particular the second virial coefficient is given as [3]:

$$B_2 = \frac{1}{2} \int_0^\infty [1 - \exp(-\beta V_{12}(r))] 2\pi r dr, \tag{3.7}$$

where $V_{12}(r)$ is the pair potential between molecules in the monolayer.

On the other hand, the density expansion of eq (3.3) leads to

$$\pi = \sigma kT \left[1 + (b_2 - \frac{a_2}{kT})\sigma + b_2^2\sigma^2 + \ldots \right] . \tag{3.8}$$

From eqs (3.6) and (3.8) we obtain to the second order term [2]:

$$b_2 - \frac{a_2}{kT} = B_2 \quad . \tag{3.9}$$

Dividing the integral (3.7) into the sum of the integrals from 0 to 2a and from 2a to infinity, where a is the radius of the adsorbate molecules, and bearing in mind that b_2 is related to the short-range part of the molecular interactions, we can write:

$$b_2 = \frac{1}{2}\int_0^2 (1 - \exp(-\beta V_{12}(r)) 2\pi r dr \tag{3.10}$$

$$\approx \frac{1}{2}\int_0^2 2\pi r dr = 2\pi a^2$$

and

$$a_2 = \frac{1}{2} kT \int_2^\infty [1 - \exp(-\beta V_{12}(r))] 2\pi r dr \approx \frac{1}{2}\int_2^\infty V_{12}(r) 2\pi r dr \tag{3.11}$$

where we have used the following inequalities valid for most gases:

$$\begin{aligned} &\text{a)} \quad \beta V_{12}(r) >> 1 \quad , \qquad \text{for} \quad r < 2a - \delta \\ &\text{b)} \quad -\beta V_{12}(r) << 1 \quad , \qquad \text{for} \quad r > 2a + \delta \end{aligned} \tag{3.12}$$

with δ small compared to a.

Another way of evaluating the coefficient a_2 is through the calculation of the isothermal change of the free energy of the van der Waals gas. With the aid of eq (3.2) we can write [5]:

$$dF = -\pi dA = \left\{ a_2 \frac{N^2}{A^2} - \frac{NkT}{A - Nb_2} \right\} dA \tag{3.13}$$

which, upon integrating, yields:

$$F = -a_2 \frac{N^2}{A^2} - NkT \log \left(1 - \frac{Nb_2}{A} \right) + F_0 \quad . \tag{3.14}$$

Equation (3.14) combined with the expression for the internal energy [2,19]:

$$E = NkT + \frac{1}{2} \frac{N^2}{A} \int d^2\underline{r}\, V_{12}(r) g(r) + NE_1 \tag{3.15}$$

where E_1 is the single molecule adsorption energy and $g(r)$ is the radial distribution function; and the thermodynamic identity:

$$F = E - TS \tag{3.16}$$

yields the following equation for a_2:

$$a_2 = -\frac{1}{2} \int_0^\infty V_{12}(r) g(r) 2\pi r dr. \tag{3.17}$$

Eq (2.17) in the low density approximation when:

$$g(r) = \begin{cases} 1 & \text{for } r > 2a \\ 0 & \text{for } r \leqslant 2a \end{cases} \tag{3.18}$$

turns into eq (3.11).

We proceed now with calculating the van der Waals coefficient a_2 using the pair potential $V_{12}(r)$ obtained in Chapter 2. To this end let us assume that the adsorbate consists of neutral, nonpolar molecules characterized by their dynamic isotropic polarizability $\alpha(\omega)$. Let the monolayer plane be determined by the centres of the adsorbed molecules and z be the distance between the monolayer and the substrate. The

substrate is a dielectric halfspace characterized by its permittivity $\varepsilon(\omega)$.

As we know from the preceding Chapter, eq (2.26), the total interaction potential $V_{12}(r)$ between two molecules at the same height above the surface consists of three terms and is given as:

$$V_{12}(r) = -\frac{3\hbar}{\pi r^6} I + \frac{8}{r^3(r^2+4z^2)^{3/2}}\left(1 - \frac{3z^2}{r^2+4z^2}\right)\frac{\hbar}{2\pi} J_1 + \\ - \frac{6}{(r^2+4z^2)^3}\frac{\hbar}{2\pi} J_2 \tag{3.19}$$

where

$$\text{a)} \quad I = \int_0^\infty \alpha^2(i\xi)d\xi$$

$$\text{b)} \quad J_1 = \int_0^\infty \alpha^2(i\xi)\frac{\varepsilon(i\xi)-1}{\varepsilon(i\xi)+1}d\xi \tag{3.20}$$

$$\text{c)} \quad J_2 = \int_0^\infty \alpha^2(i\xi)\left(\frac{\varepsilon(i\xi)-1}{\varepsilon(i\xi)+1}\right)^2 d\xi \ .$$

Substituting eq (3.19) into eq (3.11) and carrying out a simple integration we obtain [12]:

$$a_2 = \frac{3\hbar}{2^6 a^4} I - \frac{1}{16z^4}\hbar J_1\left\{\frac{1}{v(1+v^2)^{1/2}} - \frac{v}{(1+v^2)^{3/2}}\right\} + \\ + \frac{3}{2^6 z^4}\hbar J_2 \frac{1}{(1+v^2)^2} \tag{3.21}$$

where we have introduced $v = a/z$. The first term on the r.h.s. of eq (3.21) is the value of a_2 obtained when neglecting the substrate effect on the intermolecular potential. The last two terms in the above equation are the corrections due to the substrate as is readily seen from the form of the coefficients J_1 and J_2 (eqs (3.20b,c)).

Having found the 2-D van der Waals constant a_2 we may proceed with determining the critical temperature ratio $T_c(2\text{-D})/T_c(3\text{-D})$. The bulk van der Waals constants a_3 and b_3 are [5]:

$$a_3 = \frac{1}{4}\frac{\hbar}{a^3} I \quad , \qquad b_3 = \frac{16}{3}\pi a^3 \ . \tag{3.22}$$

Hence from eqs (3.5), (3.10) and (3.21) we obtain:

$$\frac{T_c(2\text{-D})}{T_c(3\text{-D})} = \frac{1}{2} - \frac{2}{3}\frac{J_1}{I}\left\{\frac{v^3}{(1+v^2)^{\frac{1}{2}}} - \frac{v^5}{(1+v^2)^{3/2}}\right\} + \frac{1}{2}\frac{J_2}{I}\frac{v^4}{(1+v^2)^2} \ . \tag{3.23}$$

Again, had the substrate effect been neglected ($J_1 = J_2 = 0$) one would have obtained the universal value of this ratio - 0.5, which was derived by Hill in 1946 [4]. To find the corrected value we need to estimate the ratios J_1/I and J_2/I. A crude method, but still good enough under these circumstances, is based upon the observation that these ratios are mean values of the quantities: $\Delta(i\xi) = [\varepsilon(i\xi)-1]/[\varepsilon(i\xi)+1]$ and $\Delta^2(i\xi)$ taken with regard to the weight $\alpha^2(i\xi)$. Since the polarizability, as a function of $i\xi$, vanishes quickly for ξ beyond the ultraviolet range, we may assert that the mean values of $\Delta(i\xi)$ and $\Delta^2(i\xi)$ are those for ξ from the visible range. It is also possible to calculate J_1 and J_2 exactly having assumed a specific model for the dielectric permittivity. The critical temperature ratio is, however, fairly insensitive to the mean value of $\Delta(i\xi)$ and $\Delta^2(i\xi)$, hence we shall not dwell on this point under these circumstances. In other words, from eqs (3.20) we can write:

$$\frac{J_1}{I} = \frac{\int_0^\infty \alpha^2(i\xi)\Delta(i\xi)d\xi}{\int_0^\infty \alpha^2(i\xi)d\xi} \approx \frac{n^2-1}{n^2+1} \tag{3.24}$$

and

$$\frac{J_2}{I} = \frac{\int_0^\infty \alpha^2(i\xi)\Delta^2(i\xi)d\xi}{\int_0^\infty \alpha^2(i\xi)d\xi} \approx \left(\frac{n^2-1}{n^2+1}\right)^2 \tag{3.25}$$

where n is the refractive index for the visible frequencies.

In the table below we have computed the values of the ratio $T_c(2\text{-}D)/T_c(3\text{-}D)$ for various dielectric permittivities and for the distance parameter $v=1$ and $v=0.9$.

Table 3.1. The critical temperature ratio: two-dimensional critical temperature to the three-dimensional critical temperature ($v = \frac{a}{z}$ - a is the radius of molecule, z is the distance from the surface).

Dielectric permittivity of adsorbent	$\varepsilon=2$	$\varepsilon=3$	$\varepsilon=4$	$\varepsilon=5$	$\varepsilon=6$	$\varepsilon=\infty$
$T_c(2\text{-}D)/T_c(3\text{-}D)$ for $v=1$	0.44	0.41	0.40	0.40	0.39	0.39
$T_c(2\text{-}D)/T_c(3\text{-}D)$ for $v=0.9$	0.49	0.42	0.41	0.41	0.40	0.40

Experimental results on the critical temperature ratio have been collected by Dash [2] . There is some spread in these values but in general it is around 0.4 and is insensitive to the kind of the substrate. The critical temperature for the liquid-vapour condensation in the *second* layer of neon adsorbed on basal plane graphite has recently been measured by Huff and Dash [20] and found to be $T_c(2\text{-}D) = 20^{\circ}K$. Interestingly, this value together with the fact that the bulk critical temperature of neon is $T_c(3\text{-}D) = 44.40^{\circ}K$ brings about the critical temperature ratio of 0.45. This would correspond (see Table 1) to the combined dielectric

constant of the monolayer plus substrate of $\varepsilon \approx 2$. Thus we have very good agreement with experiments even under quite rough approximations.

At first sight the insensitivity of the critical temperature ratio to the kind of adsorbent (especially for higher dielectric constants) is surprising. However, it arises because the correction due to the substrate represented by the last two terms of eq (3.23) consists of the terms of opposite sign, one proportional to Δ and the other to Δ^2. When Δ changes from 0 to 1 the sum remains nearly the same, as the changes of terms to a large extent cancel.

3.3 The effect of substrate topography on adsorption energies

As we mentioned in the introduction to this Chapter, the role of the surface topography on adsorption potential has long been recognized in the literature. The heat of adsorption changes with the degree of coverage for two main reasons: the influence of adsorbate-adsorbate interactions, and the existence of various energetic sites on the surface to which the gas molecules are adsorbed stronger than to "regular" places on the substrate. The active sites may be due to impurities in the crystal face of the surface, or to various topographical features of it. To the latter group belong all kinds of pores of dimensions from molecular (micropores) to those of a few microns width (macropores); as well as steps, kinks and terraces (see the review by Somorjai [21] for details).

We shall show how the dispersion formalism can be used in calculating the adsorption energies in topographically active sites on the examples of molecules adsorbed in the corner between the steps and being near the middle of the cross-section of a long micropore. In both instances we assume the substrate to be a metal of infinite conductivity. We do not attempt to present a full theory of topographically active sites but

merely indicate the method of dealing with them through the van der Waals forces formalism.

3.3.1 Molecule in a corner

From eqs (2.15) and (2.9) of Chapter 2 we see that the needed quantity is the dyadic Green's function $\underline{\underline{\mathcal{D}}}^1_B(\underline{R},\underline{R}',\omega)$ describing the reflected field in $\underline{R}$ due to an oscillating dipole $\underline{p}_0 e^{-i\omega t}$ at $\underline{R}'$. In the nonretarded approximation, which is adequate in adsorption problems we have:

$$\underline{\underline{\mathcal{D}}}^1_B(\underline{R},\underline{R}') = \nabla_{\underline{R}}\nabla_{\underline{R}'}\phi^1_B(\underline{R},\underline{R}') \tag{3.26}$$

where $\phi^1_B(\underline{R},\underline{R}')$ is the electrostatic potential due to charge density in the substrate B, which is induced by an oscillating monopole at $\underline{R}^v_0$ outside B. For a charge in the corner between the steps (Fig. 3.1) we can employ the electrostatic images method, provided the distance from the corner is much smaller than the height of the step.

It is readily seen that in this case the induced potential has the form

$$\phi^1(\underline{R},\underline{R}_0) = \frac{1}{|\underline{R}-\underline{R}_1|} - \frac{1}{|\underline{R}-\underline{R}_2|} + \frac{1}{|\underline{R}-\underline{R}_3|} \tag{3.27}$$

where $\underline{R}_1 = (x_0,y_0,0)$, $\underline{R}_2 = (-x_0,-y_0,0)$ and $\underline{R}_3 = (x_0,-y_0,0)$. The spectral density of the dispersion energy is expressed in terms of $\underline{\underline{\mathcal{D}}}^1_B$ as (cf. eq (2.15)):

$$U = -\alpha \mathrm{Tr}\underline{\underline{\mathcal{D}}}^1_B(\underline{R}_0,\underline{R}_0) \quad . \tag{3.28}$$

Substituting (3.27) into (3.28) and calculating the required trace we obtain:

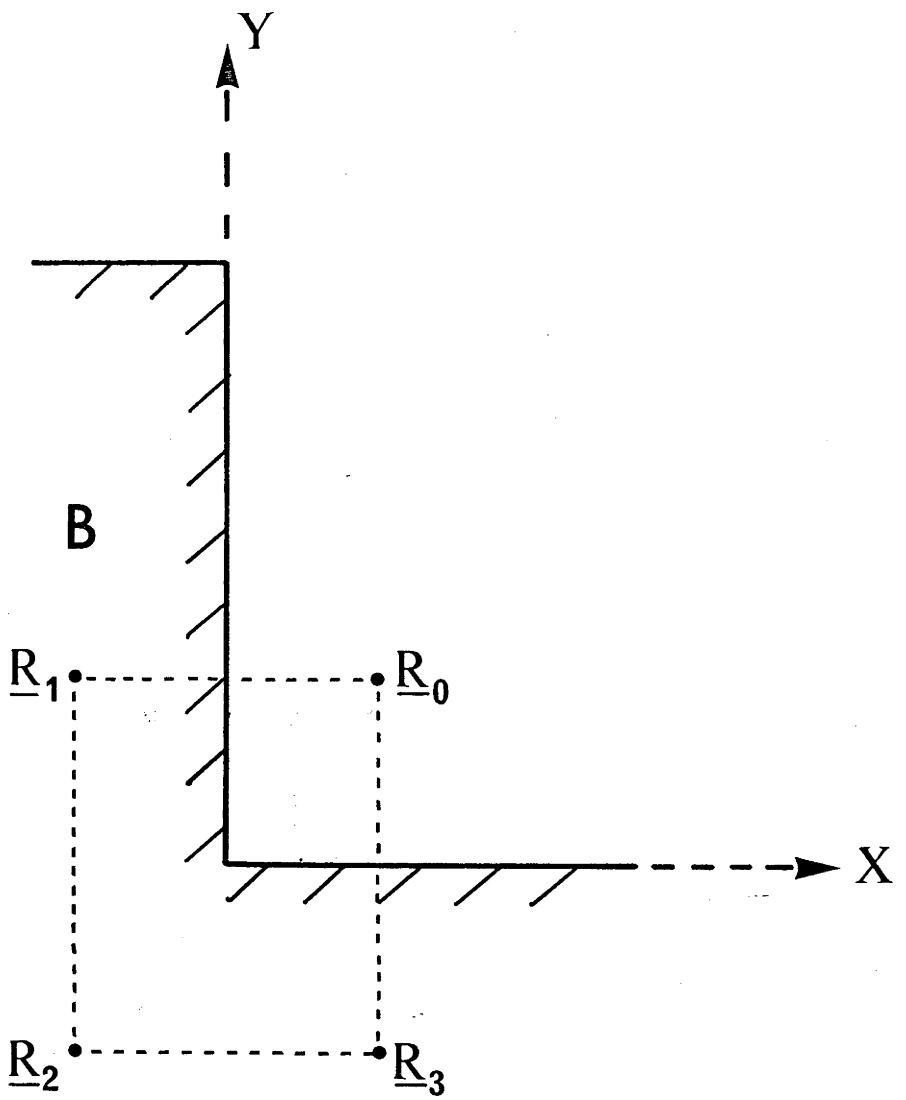

Fig. 3.1. The schematic representation of a step on the surface of adsorbent B. The z-axis is perpendicular to the plane of the drawing. The position of adsorbed molecule is $\underline{R}_0 = (x_0, y_0, 0)$; the positions of electrostatic mirror images are: $\underline{R}_1 = (x_0, y_0, 0)$, $\underline{R}_2 = (-x_0, -y_0, 0)$ and $\underline{R}_3 = (x_0, -y_0, 0)$.

$$U = -\alpha\left[\frac{1}{2x_0^3} - \frac{1}{4(x_0^2+y_0^2)^{3/2}} + \frac{1}{2y_0^3}\right] \tag{3.29}$$

When the molecule is far away from the corner $(x_0 \to \infty)$ the adsorption energy density $U(x_0 = \infty)$ becomes the same as for a homogeneous plane substrate:

$$U(x_0 = \infty) = -\frac{\alpha}{2y_0^3} \quad . \tag{3.30}$$

This compares with the adsorption energy in the corner: $(x_0 = y_0)$:

$$\frac{U(x_0 = y_0)}{U(x_0 = \infty)} = 2 - \frac{1}{4\sqrt{2}} = 1.82 \quad .$$

In other words, the adsorption energy in the corner is increased by the factor of 1.82 over that on the plane substrate.

3.3.2 Adsorption energies in micropores

In the second example we estimate the adsorption energy of a molecule in a long cylindrical micropore of arbitrary cross-section whose dimensions are small compared with a typical ultraviolet adsorption wavelength λ_0. We employ here the concept of selfenergy of the molecule due to Mahanty and Ninham [22].

Assuming that the molecule is described by a polarizability density peaked around $\underline{R}_0$: $\alpha(\underline{R}-\underline{R}_0,\omega)$, the self-energy of the molecule is defined by [22]:

$$E_{self}(\underline{R}_0) = \frac{\hbar}{2\pi}\int_0^\infty d\xi \mathrm{Tr}\int d^3\underline{R}'\alpha(\underline{R}'-\underline{R}_0,i\xi)\ \underline{\underline{\mathcal{D}}}(\underline{R}_0,\underline{R}',i\xi) \tag{3.31}$$

where $\underline{\underline{\mathcal{D}}}(\underline{R}_0,\underline{R}',\omega)$ is the dyadic Green's function for the system. In the

case when the micropore can be characterized by an infinite cylindrical waveguide (not necessarily of circular cross-section) the Green's function for Laplace's equation can be expanded as [23]:

$$\phi(\underline{R},\underline{R}_0) \approx \frac{1}{|\underline{R}-\underline{R}_0|} + \frac{2\pi|z-z_0|}{S} \tag{3.32}$$

where S is the cross-sectional area and z-axis is chosen alongside the waveguide. The dyadic Green's function can be obtained from (3.32) as $\nabla_{\underline{R}}\nabla_{\underline{R}_0}\phi(\underline{R},\underline{R}_0)$.

Taking the trace of the dyadic we obtain:

$$\mathrm{Tr}\nabla_{\underline{R}}\nabla_{\underline{R}_0}\phi(\underline{R},\underline{R}_0) = \delta(\underline{R}-\underline{R}_0) - \frac{4\pi}{S}\delta(z-z_0) \quad . \tag{3.33}$$

Combining eqs (3.33) and (3.31) yields:

$$E_{self} = \frac{\hbar}{2\pi}\int_0^\infty \alpha(0,i\xi)d\xi - \frac{2\hbar}{S}\int_0^\infty d\xi \int d^2\underline{r}\alpha(\underline{r}-\underline{r}_0,i\xi) \tag{3.34}$$

where $\underline{r}$ and $\underline{r}_0$ are lying in the cross-sectional plane defined by the centre of the molecule. The first term on the r.h.s. of eq (3.34) is the self-energy of the molecule in free space; the other is the energy due to the pore walls. We can calculate this energy assuming that the polarizability spread is Gaussian [22]

$$\alpha(\underline{R},\omega) = \alpha(\omega)\frac{1}{\pi^{3/2}a^3}e^{-R^2/a^2} \quad . \tag{3.35}$$

Assuming that the molecule is near the middle of the cross-section and that the size of the pore is greater than 2a, we can write with sufficient accuracy:

$$E_{pore} = -\frac{2}{aS\pi^{\frac{1}{2}}} \int_0^\infty \alpha(i\xi)d\xi \quad . \tag{3.36}$$

Let us compare this result with that of Mahanty and Ninham for the case of adsorption on a smooth plane [22].

$$E_{plane} = -\frac{0.16}{\pi a^3} \int_0^\infty \alpha(i\xi)d\xi \quad . \tag{3.37}$$

From eqs (3.37) and (3.36) we obtain:

$$\frac{E_{pore}}{E_{plane}} \approx 22.16 \frac{a^2}{S} \quad . \tag{3.38}$$

For a circular pore with a radius between 1.5a and 2a (thus the pore can accommodate only one molecule in its cross-section plane) we find from (3.38)

$$1.76 \leqslant \frac{E_{pore}}{E_{plane}} \leqslant 3.13 \tag{3.39}$$

which indicates a significant increase in the adsorption energy in it over that on a plane.

For larger pores, the adsorption takes place on the walls hence a full dyadic Green's function must be employed in the calculations. We shall not dwell on this part of the problem in this thesis.

3.4 Comment on van der Waals forces between heavy alkali atoms and gold surfaces

The results of experiments on van der Waals forces between alkali atoms (Cs, Rb, K) and gold surfaces published recently by Shih and Parsegian [18] do not agree with their calculations based on available theories. The smallest disagreement was found for the Lifshitz theory but even in that

case the theoretical values of the interaction potential is 60% higher than the experimental one. This is surprising because the best direct measurements of van der Waals forces between dielectric bodies do confirm the validity of the Lifshitz theory [24-29]. As a possible reason for that discrepancy, Shih and Parsegian mentioned the surface roughness, but soon dismissed it as unlikely, in view of the consistency of the results for the surfaces of gold deposited on two different substrates (steel and glass) of presumably different surface topography.

Another possible reason for this discrepancy might be connected with the fact that the dielectric response of the metal to an external electric field cannot be described by a local dielectric function; in other words, one should account for the spatial dispersivity of gold. But it can be shown [30,31] that the effect on the interaction potential due to the spatial dispersivity does not exceed 12% at the distance of 6 Å between molecules and the surface, and quickly becomes negligible as the distance increases.

It seems to us, however, that yet another surface effect may be responsible for the disagreement. The method for obtaining the gold film on the substrate is described in ref. [18]. The gold film is evaporated from wires wrapped around a tungsten heater 8 inches away from the substrate. It is known [32-35] that the gold film obtained by a vacuum deposition forms a kind of aggregate of small metal particles, rather than a uniform medium. The particles in the thinnest films are very small (20 Å in diameter) and almost spherical, whilst in thick films they are bigger (400 Å in diameter) and of irregular shape [32] . The optical constants of such aggregated films are different from those of the bulk metal and the first theoretical explanation was given by Maxwell-Garnett in 1904 [36]. Thus it seems to be important to investigate how this affects van der Waals interactions between such films and other

bodies. To see this, note that the spectral density of the van der Waals energy of interaction between the film and another body separated by a vacuum is, in the linear approximation, proportional to the quantity:

$$\Delta_f(i\xi) = (\varepsilon_f(i\xi) - 1)/(\varepsilon_f(i\xi) + 1) , \tag{3.40}$$

where $\varepsilon_f(i\xi)$ is the dielectric constant for the film at the imaginary frequency $i\xi$. In the experiment under discussion the energy of interaction between an atom, characterized by the dynamic polarizability $\alpha(\omega)$ and a film distance r from it is given by the formula (we assume for simplicity the non-retarded approximation, $c \to \infty$) [18]:

$$V_f(r) = -\frac{kT}{2r^3} \sum_{n=0}^{\infty}{}' \alpha(i\xi_n)\Delta_f(i\xi_n) , \tag{3.41}$$

where k is Boltzmann's constant and $\xi_n = (2kT\pi/\hbar)n$. The prime on the summation means that the $n=0$ term is multiplied by half.

Let us assume that the aggregated film is formed by small spheres, densely packed in a regular or completely random array. The effective dielectric constant for such medium can be found from the familiar Lorentz-Lorenz formula:

$$(\varepsilon_f - 1)/(\varepsilon_f + 2) = F(\varepsilon - 1)/(\varepsilon + 2), \tag{3.42}$$

where F is the volume fraction of the spheres and ε is their dielectric constant (taken here to be equal to the dielectric constant of the bulk metal). From (3.42) it follows that

$$\Delta_f \equiv \frac{\varepsilon_f - 1}{\varepsilon_f + 1} = \frac{3F}{2 + F} \frac{\varepsilon - 1}{\varepsilon + (4-F)/(2+F)} \tag{3.43}$$

In the r.h.s. term of (3.43) we can replace (4-F)/(2+F) by 1 in the denominator; the relative error in the worst case when $\varepsilon=1$ being $\frac{1}{3}(1-F)$. Now from eqs (3.43) and (3.41) we obtain

$$V_f(r) = -\frac{3F}{2+F}\left(\sum_{n=0}^{\infty}{}' \frac{\varepsilon(i\xi_n)-1}{\varepsilon(i\xi_n)+1}\,\alpha(i\xi_n)\right)\frac{kT}{2r^3} \equiv \frac{3F}{2+F}\,V(r)\ , \tag{3.44}$$

where $V(r)$ is the value of the potential in the case of the uniform film characterized by the bulk dielectric constant $\varepsilon(i\xi)$. Assuming now that the value V_f is the one obtained from the Shih-Parsegian experiment we find the needed volume fraction of the spheres in the aggregated film: $F = 0.51$. This value compares with $F = 0.52$ for the cubic close packed array of spheres.

One can also consider other shapes of the particles and/or calculate the interaction potential between the molecule and a composite medium consisting of a layer of the particles and the bulk gold underneath. It proves that the accounting for the bulk gold under the film will not change the calculated value of the potential by more than 10% so long as the thickness of the film is greater than 1.6 times the distance r.

Obviously the above analysis is a simplification. It shows, however, that the disagreement between the experimental values for the aggregated film and the theoretical calculations for the uniform film can be explained by taking due account of the fact that the dielectric constants for the two cases are not the same.

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CHAPTER 4

VAN DER WAALS FORCES BETWEEN MOVING BODIES

4.1 Introduction

The theory of dispersion forces has only been developed for interactions in equilibrium. Therefore van der Waals forces between bodies in motion cannot be predicted properly from the formalism described in Chapter 1, since one cannot talk about the equilibrium in a system whose parts move with respect to each other (although one may have a steady state).

Clearly, there is a need to extend the van der Waals forces formalism to the case of moving bodies, if only for the reason of estimating the impact that motion has on dispersion interactions. To our knowledge, there has been only one attempt to tackle this problem; considering the example of two semi-infinite dielectric media travelling parallel to each other, Teodorovich [1] found that apart from the normal component of the van der Waals force between the bodies there exists also a tangential force of nonconservative character. In his terminology we shall call it the frictional force.

Teodorovich's approach is based on equilibrium theory (through the application of the fluctuation-dissipation theorem) and one may question the validity of his calculation. Here we shall attempt to present an alternative approach (which, we believe, is more transparent than the original one) using the problem of a molecule moving parallel to the surface of a semi-infinite substrate as an example. We shall treat the substrate as spatially dispersive and obtain the results for dielectrics as a special limit.

The existence of a frictional component of the van der Waals force between a moving molecule and a substrate is a manifestation of the general phenomenon of dissipation of electromagnetic energy in condensed media. One distinguishes several loss mechanisms: e.g. excitation of plasmons, interband transitions and ionization of the constituent molecules. We shall not be concerned with the detailed physical description of particular loss mechanisms and assume simply that they are subsumed in specific representations for dielectric permittivities. We refer here to the Appendix at the end of this Chapter.

As an introduction to the main problem we consider first frictional forces acting on a moving charge and dipole near a metallic surface. This is done in Sections 4.2 and 4.3. Section 4.4 is devoted to the case of moving molecule.

4.2 Loss of kinetic energy of a charge moving parallel to a vacuum-metal interface.

The measurements of energy losses of charged particles colliding with solids have long been used in solid state physics to determine the properties of metals and semiconductors [2]. Therefore, the theoretical problem of the interaction between a moving charge and a solid substrate has been treated rather extensively [3-7]. The discussion of results in this area is in a context different from that which we are interested in here, and it seems worthwhile to consider the problem from the beginning in the light of its relevance to frictional dispersion forces.

Our aim is to calculate the self-force acting on a moving charge due to the induced surface charge density at the interface between a metallic, or dielectric half-space, and a vacuum. We shall need, therefore, the potential due to this surface charge, which for brevity is

called the induced potential. The total potential is the sum of the potential of the isolated charge plus the induced potential.

Let us choose the coordinate system such that the region $z < 0$ is occupied by the medium while the region for $z > 0$ is a vacuum. Consider a fictitious oscillating monopole with frequency ω_0, i.e. $Q \exp(-i\omega_0 t)$ (for a real point charge we let $\omega_0 = 0$) which is travelling with the velocity $\underline{v} = (v,0,0)$ at a fixed distance z_0 from the surface. We shall assume that the velocity is small enough to neglect relativistic effects and that the frequency ω_0 satisfies the inequality: $\omega_0 << 2\pi c/z_0$. Both assumptions justify the use of quasistatic approximation, in which the electric field of the moving charge is derived from the scalar potential $\phi(\underline{R},t)$. Let $\underline{R} = (\underline{r},z)$, where $\underline{r}$ lies in the xy plane and let $\rho(\underline{r},z,t)$ be an arbitrary charge density outside the substrate, i.e. $z > 0$. Let us define the spectral intensity $\rho(\underline{R},\omega)$ by

$$\rho(\underline{R},t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\omega \exp(-i\omega t)\rho(\underline{R},\omega) \quad . \tag{4.1}$$

Denote by $\phi_0^i(\underline{R},\underline{R}',\omega)\exp(-i\omega t)$ the induced potential of a unit oscillating monopole resting at $\underline{R}' = (\underline{r}',z')$, $z > 0$. From (4.1) the induced potential of the charge density $\rho(\underline{R},t)$ is therefore:

$$\phi^1(\underline{R},t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} \int d^3\underline{R}' \rho(\underline{R}',\omega)\phi_0^i(\underline{R},\underline{R}',\omega) \quad . \tag{4.2}$$

The moving oscillating monopole is described by the charge density:

$$\rho(\underline{r},z,z_0,t) = Qe^{-i\omega_0 t}\delta(\underline{r} - \underline{v}t)\delta(z - z_0) \quad . \tag{4.3}$$

Applying the 2-D space Fourier transform with respect to $\underline{r}$, and also the Fourier transform with respect to t in the above equation we obtain:

$$\rho(\underline{k},z,z_0,\omega) = 2\pi Q\delta(\underline{k}\cdot\underline{v} + \omega_0 - \omega)\,\delta(z-z_0) \tag{4.4}$$

where $\underline{k}$ is the 2-D wavevector. On the other hand Fourier transforming with respect to $\underline{r}$ in eq (4.2) yields:

$$\phi^1(\underline{k},z,t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega e^{-i\omega t}\int_{-\infty}^{+\infty} dz'\rho(\underline{k},z',\omega)\phi_0^i(\underline{k},z,z';\omega). \tag{4.5}$$

From eqs (4.4) and (4.5) we obtain:

$$\phi^1(\underline{k},z,z_0,t) = Q\phi_0^i(\underline{k},z,z_0,\underline{k}\cdot\underline{v} + \omega_0)e^{-i\underline{k}\cdot\underline{v}\,t}\; e^{-i\omega_0 t} \quad . \tag{4.6}$$

By taking the inverse Fourier transform with respect to $\underline{k}$ we find from (4.6) the induced potential of the moving monopole:

$$\phi^1(\underline{r},z,z_0,t) = \frac{Qe^{-i\omega t}}{(2\pi)^2}\int d^2k e^{i\underline{k}\cdot(\underline{r} - \underline{v}t)}\phi_0^i(\underline{k},z,z_0,\underline{k}\cdot\underline{v} + \omega_0) \quad . \tag{4.7}$$

In the coordinate system moving with the charge the potential depends on the time only through the factor $e^{-i\omega_0 t}$. If we choose the origin of the new coordinate system such that the position of the charge is $\underline{R}_0 = (0,0,z_0)$, the vector $\underline{r}$ becomes: $\underline{r} + \underline{v}t$ and from (4.7) we obtain:

$$\phi^1(\underline{r},z,z_0,t) = \frac{Qe^{-i\omega_0 t}}{(2\pi)^2}\int d^2\underline{k} e^{i\underline{k}\cdot\underline{r}}\phi_0^i(\underline{k},z,z_0,\underline{k}\cdot\underline{v} + \omega_0) \quad . \tag{4.8}$$

Note that eq (4.8) is already given in the new coordinate system.

We shall now apply the above result to the case of a static charge ($\omega_0 = 0$). The force exerted on a probe charge q travelling with the same velocity $\underline{v}$, or in other words, resting in the new coordinate system, at $\underline{R} = (\underline{r},z)$, follows as

$$\underline{F} = -q \nabla_{\underline{R}} \phi^1(\underline{R}, z_0) \quad . \tag{4.9}$$

Thus the force acting on the source charge itself (through the induced charge density in the substrate) is obtained as the limit:

$$\begin{aligned} \underline{F} &= -Q^2 \lim_{\underline{R}\to\underline{R}_0} \phi(\underline{R},\underline{R}_0) = -\frac{Q^2}{(2\pi)^2} \lim_{\underline{R}\to\underline{R}_0} \int d^2\underline{k} e^{i\underline{k}\underline{r}} \phi_0^i(\underline{k}, z, z_0, \underline{k}\underline{v}) \\ &= -\frac{Q^2 i}{(2\pi)^2} \int k_x \phi_0^i(\underline{k}, z_0, z_0, \underline{k}\cdot\underline{v}) d^2\underline{k} \quad . \end{aligned} \tag{4.10}$$

It is evident from the symmetry of the problem that for an isotropic substrate, which we shall assume to be the case here, only the X and Z components of the force can be different from zero. When v=0, then also the X-component of the force, F_x, disappears because the potential $\phi(\underline{k}, z, z', \omega)$ depends only on the absolute value of the vector $\underline{k}$, $k = |\underline{k}|$. In general, however, the F_x component will be different from zero for $v \neq 0$, and represent the frictional force responsible for the loss of kinetic energy of the particle.

Before proceeding further we note that the force $F_x(v)$ treated as a function of v need not be analytic at v=0; and cannot therefore be approximated by the Taylor expansion about v=0. As we shall see later this is the case only when the substrate has very sharp and narrow absorption peaks. For the moment, however, let us assume that the force can be expanded in powers of the velocity v, and define the frictional coefficient as:

$$\kappa = -\left.\frac{\partial F_x}{\partial v}\right|_{v=0} \tag{4.11}$$

so that to the leading order we can write

$$F_x = -\kappa v \quad . \tag{4.12}$$

We shall now choose the polar coordinate system in the $\underline{k}$-plane such that the angle between $\underline{k}$ and $\underline{v}$, and hence also between $\underline{k}$ and the x-axis, is ψ. We then have $k_x = k\cos\psi$ and $\underline{k}\cdot\underline{v} = kv\cos\psi$. Making these substitutions into eq (4.10) and then (4.11) we obtain

$$\kappa = -\frac{Q^2}{4\pi}\frac{1}{i}\frac{\partial}{\partial v}\int_0^\infty k^2 dk \int_0^{2\pi} \phi_0^i(k,z_0,z_0,kv\cos\psi)\cos\psi d\psi \Bigg|_{v=0} \tag{4.13}$$

$$= \frac{Q^2}{4\pi}\int_0^\infty k^3 dk \frac{\partial}{\partial \xi}\phi_0^i(k,z_0,z_0,i\xi)\Bigg|_{\xi=0}$$

where we have used the fact that $\phi_0^i(\underline{k},z,z',\omega)$ depends on the absolute value of $\underline{k}$ and introduced the variable $\xi = -ikv$.

We shall now make use of the form of the induced potential which has been derived in Chapter 2 (eq (2.40)). Modifying eq (2.40) to the present notation we see that the 2-D Fourier transform of the induced potential, $\phi_0^i(k,z,z_0,i\xi)$, is given as

$$\phi_0^i(k,z,z_0,i\xi) = -\frac{2\pi}{k}e^{-k(z+z_0)}\, S(k,i\xi) \tag{4.14}$$

where $S(k,i\xi)$ is determined, for the hydrodynamic model of the metal, by eq (2.50). Differentiating eq (2.50) with respect to ξ yields

$$\frac{\partial\phi_0^i}{\partial\xi}\Bigg|_{\xi=0} = -\frac{2\pi}{\omega_p^2}\frac{e^{-2kz_0}}{k}\frac{(\frac{3}{2}\beta k\omega_p^2 + \beta^3k^3 - (\omega_p^2+\beta^2k^2)^{3/2})}{(\omega_p^2+\beta^2k^2)^{\frac{1}{2}}[(\omega_p^2+\beta^2k^2)^{\frac{1}{2}}+\beta k]^2}\,\gamma\,. \tag{4.15}$$

As in Chapter 2, it is convenient to introduce the dimensionless parameter μ, and the variable x:

$$\text{a)}\quad \mu = \beta/2z_0\omega_p\,, \qquad \text{b)}\quad x = 2kz_0\,. \tag{4.16}$$

With this notation, from eqs (4.15) and (4.13) we arrive at the following

representation for the frictional coefficient

$$\kappa = -\frac{Q^2\gamma}{\omega_p^2(2z_0)^3}\int_0^\infty x^2 e^{-x}\,\frac{\frac{3}{2}\mu x + \mu^3x^3 - (1+\mu^2x^2)^{3/2}}{(1+\mu^2x^2)^{1/2}[(1+\mu^2x^2)^{1/2}+\mu x]^2}\,dx \quad . \tag{4.17}$$

It can be shown that the integrand is always negative for $0 < x < \infty$, hence the frictional coefficient is always positive, as it should. When μ increases the κ decreases, so that the spatial dispersion has the effect of reducing the frictional force. For small μ, i.e. small β and/or large z_0, we obtain an asymptotic expression [8]:

$$\kappa = \frac{Q^2\gamma}{\omega_p^2(2z_0)^3}\left[1 - \frac{21}{4}\frac{\beta}{\omega_p z_0} + \frac{15}{2}\frac{\beta^2}{\omega_p^2 z^3} + \ldots\right] . \tag{4.18}$$

For large μ (i.e. small z_0 and/or large β) the appropriate asymptotic form is [8]

$$\kappa = \frac{3}{64}\frac{\gamma Q^2}{\beta\omega_p}\cdot\frac{1}{z_0^2} \quad . \tag{4.19}$$

Thus for small distances z_0 the force behaves like $1/z_0^2$, whilst for large z_0 it decays like $1/z_0^3$.

For small γ eq (4.13) is useless since the force is badly approximated by the power series of v. This is due to the fact that the poles of the function $\phi_0^i(k,z,z_0,\omega)$ on the complex ω-plane lie close to the real axis and the contribution from them to the integral in eq (4.10) becomes dominant. To examine the limit of small γ assume that spatial dispersion is not significant, i.e. let $\beta=0$, and write the potential $\phi_0^i(k,z,z_0,\omega)$ as

$$\phi_0^i(k,z,z_0,\omega) = -\frac{2\pi}{k}e^{-k(z+z_0)}\Delta(\omega) \tag{4.20}$$

where

$$\Delta(\omega) \equiv S(k,\omega)\Big|_{\beta=0} = \frac{\omega^2}{\omega_s^2 - i\gamma\omega - \omega^2} \tag{4.21}$$

and $\omega_s^2 \equiv \frac{1}{2}\omega_p^2$.

The poles of $\Delta(\omega)$ are

$$\omega_j = -\frac{i\gamma}{2} \pm \sqrt{\omega_s^2 - \frac{1}{4}\gamma^2} \quad , \qquad j = 1,2 \tag{4.22}$$

and as $\gamma \to 0$ they approach $\omega_k = \pm\omega_s$. Let us introduce these variables into eq (4.10):

$$u = k_x v \ , \qquad y = k_y v \ . \tag{4.23}$$

With the potential given by eq (4.20) we can transform (4.10) into:

$$F_x = \frac{Q^2}{2\pi i v} \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} du \, \frac{u \exp\left(-\frac{2z_0}{v}\sqrt{u^2+y^2}\right)}{\sqrt{u^2+y^2}} \cdot \frac{\omega_s^2}{\omega_s^2 - i\gamma u - u^2} \ . \tag{4.24}$$

Representing the last factor of the integrand by the sum of partial fractions and making use of the formula

$$\lim_{\gamma \to 0^+} \frac{1}{\omega - \omega_j + i\gamma} = -\pi i \delta(\omega - \omega_j) + P\,\frac{1}{\omega - \omega_j} \tag{4.25}$$

we can see that in the limit of $\gamma = 0$ the force becomes:

$$F_x = -\frac{Q^2\omega_s^2}{v^2} \int_0^{\infty} \frac{\exp\left(-\frac{2z_0}{v}\sqrt{\omega_s^2+y^2}\right)}{\sqrt{\omega_s^2+y^2}}\, dy \tag{4.26}$$

$$= -\frac{Q^2\omega_s^2}{v^2} \, K_0\left(\frac{2z_0\omega_s}{v}\right)$$

where K_0 is the modified Bessel function of the zeroth order.

This result was obtained by Takimoto [4] and Muscat and Newns [7]. Now we can clearly see why the expansion in the power series of $F_x(v)$ does not work in the case $\gamma=0$. When $v \to 0$ the force (eq (4.26)) vanishes and

$$F_x \sim ( ) \frac{1}{v^2} \exp(-2z_0\omega_s/v) \tag{4.27}$$

and all its derivatives with respect to v disappear for $v=0$. It follows then that the power expansion around $v=0$ is not useful in this case, as it is generally for the case of a function infinitely differentiable (at $v=0$) and nonanalytic at the same time.

The physical interpretation of the loss formalism when $\gamma=0$ is seen from eq (A4.9) of the Appendix. In practice γ is never exactly zero; but as it becomes very small, the absorption peak around $\omega = \omega_s$ is rendered sharp and narrow. The loss of energy of an electromagnetic field whose frequency spectrum covers ω_s then becomes independent of γ.

Let us estimate the magnitude of the frictional force in a typical case. For good conductors, such as copper or aluminium, the half-width of the absorption peak γ is very small. For Al the ratio $\gamma/\omega_p \equiv \omega_p/\sigma$, where σ is the conductivity, is of the order of 10^{-3}. In view of this we shall use eq (4.26) rather than the frictional coefficient for calculating the force. Consider an electron moving with a velocity corresponding to the kinetic energy of 100 eV. We choose the atomic units system in which $\hbar = e = m_e = 1$, hence 100 eV is equivalent to 3.67 atomic units (a.u.) and the velocity $v = 2.71$ a.u. For Al we have $\omega_p = 0.565$ a.u. and thus $\omega_s = \frac{1}{\sqrt{2}} \omega_p = 0.40$ a.u. With these values eq (4.26) yields the following dependence of the frictional force on the distance

z_0 between the electron and the surface:

$$F_x(z_0) = -0.0218\ K_0\ (0.3 \times z_0) \quad [\text{a.u.}]. \tag{4.28}$$

For a distance $z_0 = 4$ a.u. (≈ 2 Å) the force equals 0.007 a.u. This compares with the force of electrostatic image attraction between the metal and an electron at rest at the same distance ($F_z = -1/(2z_0)^2$) of 0.016 a.u. Frictional force is then quite significant and one can see its effect in suitably designed experiments [4].

4.3 The case of a moving dipole

We wish now to extend the theory laid down in the preceding section to the case of a moving oscillating dipole. The difference between the present and previous problem is that we need now the induced (or, as it may be called, reflected or scattered) field due to the interface with the moving dipole as a source. This field is given by the dyadic Green's function $\underline{\underline{D}}^1(\underline{R}_1, \underline{R}_0, \omega)$ (see Chapter 2, eq (2.16)) which in the nonretarded approximation can be obtained from the induced potential:

$$\underline{\underline{D}}^1(\underline{R}_1, \underline{R}_0; \omega) = \nabla_{\underline{R}_1} \nabla_{\underline{R}_0}\ \phi^1(\underline{R}_1, \underline{R}_0, \omega) \tag{4.29}$$

$$= \left(-\nabla_{\underline{r}}\ \nabla_{\underline{r}} + \underline{e}_z \underline{e}_z \frac{\partial^2}{\partial z_1 \partial z_0}\right) \phi^1(\underline{r}, z_1, z_0; \omega)$$

where $\underline{e}_z$ is the unit vector in the Z-direction, $\underline{r} = \underline{r}_1 - \underline{r}_0$, and we have used dyadic notation.

Now assume that the dipole $\underline{p}e^{-i\omega_0 t}$ is travelling with the velocity $\underline{v} = (v,0,0)$ at the height z_0 above the surface. In the coordinate system associated with the dipole the dyadic $\underline{\underline{D}}^1$ is obtained by differentiating eq (4.8)

$$\underline{\underline{D}}^1(\underline{r},z,z_0,\omega_0) = \frac{1}{(2\pi)^2}\int d^2\underline{k}\left\{\underline{k}\,\underline{k} + \underline{e}_z\underline{e}_z\frac{\partial^2}{\partial z\partial z_0}\right\}\phi_0^i(\underline{k},z,z_0,\underline{k}\cdot\underline{v}+\omega_0)\ . \quad (4.29a)$$

A probe dipole $\underline{p}'e^{-i\omega_0 t}$ at $\underline{R} = (\underline{r},z)$ has the mean energy (averaged over the period $T = 2\pi/\omega_0$) in the induced field of the source dipole (see A4.4):

$$U(\underline{R},\underline{R}_0,\omega_0) = -\frac{1}{2}\,\mathrm{Re}(\underline{p}'\cdot\underline{\underline{D}}^{1*}(\underline{R},\underline{R}_0,\omega_0)\underline{p}^*) \quad (4.30)$$

Thus the mean force acting on the probe can be written as:

$$\underline{F}(\underline{R},\underline{R}_0,\omega_0) = -\frac{1}{2}\,\nabla_{\underline{R}}\,\mathrm{Re}(\underline{p}'\cdot\underline{\underline{D}}^{1*}(\underline{R},\underline{R}_0;\omega_0)\underline{p}^*). \quad (4.31)$$

The frictional force follows from (4.31) as the X-component of $\underline{F}$ in the limit $\underline{p}' \to \underline{p}$ and $\underline{R} \to \underline{R}_0$:

$$F_x(z_0,\omega_0) = -\lim_{\underline{R}\to\underline{R}_0}\left(+\frac{1}{2}\,\mathrm{Re}\,\frac{\partial}{\partial x}\,(\underline{p}\cdot\underline{\underline{D}}^{1*}(\underline{R},\underline{R}_0;\omega_0)\underline{p}^*)\right|_{x=0}\ . \quad (4.32)$$

4.4 Van der Waals frictional forces

Finally consider a moving molecule characterized by the dynamic polarizability $\alpha(\omega)$. We limit ourselves to isotropic molecules, but the method can be extended to anisotropic polarizabilities in a simple manner. The quantum-mechanical system which we shall consider consists of the molecule plus the electromagnetic field. The reference system is such that the molecule rests in it, the whole effect of the motion is contained in the electromagnetic field. The advantage of such reference system is that the Hamiltonian of interaction between the molecule and the field does not depend on time explicitly, since for a

constant velocity $\underline{v}$ the electromagnetic field is independent of time. This feature makes possible the use of the fluctuation-dissipation theorem.

As in Chapter 1, we shall employ the coupling parameter formalism. This time, however, we wish to find the force due to the coupling between the molecule and the reflected, or induced, electric field $\underline{E}^1$. We start from introducing the fictitious Hamiltonian $H(\lambda)$:

$$H(\lambda) = H_0 - \lambda \underline{P} \cdot \underline{E}^1(\underline{R}_0) \quad , \quad H(1) = H \tag{4.33}$$

where $\underline{P}$ is the polarization operator for the molecule, and the position of the molecule $\underline{R}_0$ enters as a parameter. The i-th component of the force acting on the molecule from the field $\underline{E}^1$ can be expressed as the coupling constant integral:

$$F_i = \left\langle \frac{\partial H}{\partial R_i} \right\rangle \Big|_{\underline{R}=\underline{R}_0} = - \int_0^1 \frac{d\lambda}{\lambda} \left\langle \lambda \underline{P} \cdot \frac{\partial \underline{E}}{\partial R_i} \right\rangle_\lambda \Big|_{\underline{R}=\underline{R}_0} \tag{4.34}$$

where, as in Chapter 1, the subscript λ means that the average is taken with regard to the Hamiltonian $H(\lambda)$. We shall now absorb the parameter λ in the polarization operator by replacing the electronic charge e by $e' = \lambda e$, and suppress the λ-dependence in the following derivation.

With the notation:

$$E_{i,j} = \frac{\partial E_i}{\partial R_j} \Big|_{\underline{R}=\underline{R}_0} \tag{4.35}$$

we can write:

$$\left\langle \underline{P} \cdot \frac{\partial \underline{E}}{\partial R_j} \right\rangle = \sum_{i=1}^{3} \langle P_i E_{i,j} \rangle = \sum_{i=1}^{3} \langle E_{i,j} P_i \rangle \tag{4.36}$$

where the last step follows from the fact that $E_{i,j}$ and P_i are

Hermitian, and the average value $\langle \underline{P} \cdot \frac{\partial \underline{\underline{E}}}{\partial R_j} \rangle$ is real. The mean value $\langle E_{i,j} P_i \rangle$ can be expressed in terms of the statistical Green's function $G_{E_{i,j}P_i}(i\xi)$ as (see Chapter 1 eq (1.85)):

$$\langle E_{i,j} P_i \rangle = -\frac{2}{\beta} \sum_{n=0}^{\infty}{}' G_{E_{i,j}P_i}(i\xi_n) , \quad \xi_n = 2\pi nkT/\hbar \quad . \tag{4.37}$$

We need now to interpret the Green's function $G_{E_{i,j}P_i}$. In general, the Green's function $G_{AB}(t)$ is the deviation in the mean value of the quantity A, at time t, caused by an impulsive force applied to the system at t=0, such that the energy input which occurred is described by the addition of the term:

$$H' = -B\delta(t) \tag{4.38}$$

to the Hamiltonian. In our case $B \equiv P_i$, the i-th component of the dipole moment of the molecule, hence the impulsive force conjugated with $\underline{P}_i$ is the electric field $\delta\underline{E} = \underline{n}_i \delta(t)$, where $\underline{n}_i$ is the unit vector in the i-th direction. Going over to Fourier components of the Green's functions we can interpret the function $G_{E_{i,j}P_i}(\omega)$ as the mean value of the derivative $E_{i,j}(\underline{R}_0)$ caused by the oscillating unit field $\underline{n}_i e^{-i\omega t}$ applied to the molecule (the equilibrium average of the field $\underline{E}$ and hence its derivatives is zero). But the unit oscillating field $\underline{n}_i e^{-i\omega t}$ develops the mean dipole moment on the molecule: $\underline{p}(\omega) = \underline{n}_i \alpha(\omega)$, thus the mean electric field $\underline{E}^1(\underline{R})$ can be found from the macroscopic Green's dyadic $\underline{\underline{D}}^1(\underline{R},\underline{R}_0,\omega)$ as

$$\langle E_i{}^1(\underline{R}) \rangle = D^1_{ii}(\underline{R},\underline{R}_0,\omega)\alpha(\omega) \tag{4.39}$$

where we have neglected the multipole coupling between the molecule and the field. Differentiating both sides of eq (4.49) with respect to R_j,

and using the fact that averaging and differentiating with respect to a parameter commute, we get

$$G_{E_{i,j}P_i}(i\xi) \equiv \langle E_{i,j}(\underline{R}_0)\rangle = \lim_{\underline{R}\to\underline{R}_0} \frac{\partial D^1_{ii}(\underline{R},\underline{R}_0,i\xi)}{\partial R_j}\alpha(i\xi) \quad . \tag{4.40}$$

Now from eqs (4.40), (4.37) and (4.36) we obtain

$$\left\langle \underline{P}\cdot\frac{\partial \underline{\underline{E}}}{\partial R_j}\right\rangle\Big|_{\underline{R}=\underline{R}_0} = -\frac{2}{\beta}\sum_{n=0}^{\infty}\lim_{\underline{R}\to\underline{R}_0}\frac{\partial}{\partial R_j}\mathrm{Tr}D^1(\underline{R},\underline{R}_0,i\xi_n)\alpha(i\xi_n) \quad . \tag{4.41}$$

Reintroducing the parameter λ in the above equation and bearing in mind that the polarizability is proportional to e^2 and hence to λ^2, we can perform the integration in eq (4.34) to obtain:

$$F_j = -\frac{1}{\beta}\lim_{\underline{R}\to\underline{R}_0}\frac{\partial}{\partial \underline{R}_j}\sum_{n=0}^{\infty}{}' \mathrm{Tr}\underline{\underline{D}}^1(\underline{R},\underline{R}_0,i\xi_n)\alpha(i\xi_n) \tag{4.42}$$

$$\equiv -\frac{1}{\beta}\sum_{n=0}^{\infty}{}' W_j(i\xi_n)$$

where we have introduced the function $W_j(i\xi)$ by:

$$W_j(i\xi) = \lim_{\underline{R}\to\underline{R}_0}\frac{\partial}{\partial \underline{R}}\mathrm{Tr}\underline{\underline{D}}^1(\underline{R},\underline{R}_0,i\xi_n)\alpha(i\xi_n) \quad . \tag{4.43}$$

As in the preceding sections we shall assume that the velocity of the molecule is $\underline{v} = (v,0,0)$, hence only the F_x component of the tangential force will be different from zero. Its spectral intensity $W_x(i\xi)$ is readily obtained from (4.43) and (4.29a):

$$W_x(v,i\xi) = -\frac{i}{\pi}\int d^2\underline{k}\, k_x k e^{-2kz_0} S(k,\underline{k}\cdot\underline{v}+i\xi)\alpha(i\xi) \quad . \tag{4.44}$$

For $\xi > 0$ the integrand in the above expression is free

from singularities even when $\gamma=0$. The contribution from the singularities of $S(k,\omega)$ (if any) will only be significant when the $\xi = 0$ term in the expression for the force (4.42) becomes dominant, which takes place at high temperatures. Putting aside an appropriate analysis of this case till the end of the section we proceed to calculate the frictional coefficient κ^1 defined by:

$$\kappa^1 = - \frac{\partial F_x}{\partial v}\bigg|_{v=0} = \frac{1}{\beta} \sum_{n=0}^{\infty}{}' \frac{\partial W_x(v,i\xi_n)}{\partial v}\bigg|_{v=0} . \tag{4.45}$$

From (4.44) we get

$$\frac{\partial W_x}{\partial v}\bigg|_{v=0} = - \frac{1}{\pi} \int d^2\underline{k}\, k_x^2 k e^{-2kz_0} \frac{\partial S(k,i\xi)}{\partial \xi} \alpha(i\xi) . \tag{4.46}$$

For small temperatures T we may replace the summation over the frequencies ξ_n by an integral. The sum $\frac{1}{\beta} \sum_{n=0}^{\infty}{}'$ becomes then the integral $\frac{\hbar}{2\pi} \int_0^\infty d\xi$, and from eqs (4.45), (4.46) we obtain:

$$\kappa^1 = - \frac{\hbar}{2\pi} \int_0^\infty \alpha(i\xi) d\xi \int_0^\infty k^4 e^{-2kz_0} \frac{\partial S(k,i\xi)}{\partial \xi} . \tag{4.47}$$

Performing integration by parts with respect to ξ in (4.47) we arrive at

$$\kappa^1 = \frac{\hbar}{2\pi} \int_0^\infty d\xi \frac{\partial \alpha}{\partial \xi} \int_0^\infty k^4 e^{-2kz_0} S(k,i\xi) + \tag{4.48}$$

$$+ \frac{\hbar}{2\pi} \alpha(0) \int_0^\infty k^4 e^{-2kz_0} S(k,0) .$$

Let us assume that the polarizability $\alpha(i\xi)$ is given by

$$\alpha(i\xi) = \frac{\alpha_0}{1 + \xi^2/\omega_0^2} \tag{4.49}$$

where ω_0 is a typical ultra-violet frequency ($2 \times 10^{16} s^{-1}$). Using the parameter μ and the variable x as defined by eqs (4.16), and introducing dimensionless quantities:

$$\text{a)} \quad \Gamma = \gamma/\omega_p \,, \qquad \text{b)} \quad \eta = \omega_p/\omega_0 \tag{4.50}$$

we can transform eq (3.48) into the form:

$$\begin{aligned} \kappa^1 = \frac{\alpha_0 \hbar}{(2z_0)^5 \pi} \Bigg\{ & - \eta^2 \int_0^\infty d\zeta \, \frac{\zeta}{(1+\eta^2\zeta^2)^2} \\ & \times \int_0^\infty x^4 e^{-x} \, \frac{(\zeta^2+\Gamma\zeta+1+\mu^2x^2)^{\frac{1}{2}} - \mu x \quad dx}{(1+2(\zeta^2+\Gamma\zeta)\,(\zeta^2+\Gamma\zeta+1+\mu^2x^2)^{\frac{1}{2}} + \mu x} \\ & + \frac{1}{2} \int_0^\infty x^4 e^{-x} \, \frac{(1+\mu^2x^2)^{\frac{1}{2}} - \mu x}{(1+\mu^2x^2)^{\frac{1}{2}} + \mu x} \, dx \Bigg\} \quad . \end{aligned} \tag{4.51}$$

The above equation is the main result of this section. It gives the frictional coefficient for a molecule moving parallel to a spatially dispersive substrate.

The effect of the spatial dispersion on the frictional coefficient is through the parameter μ. As μ increases, the κ^1 decreases, so that in order to estimate an upper limit of the frictional force in a typical case we may put $\mu=0$. Also, for good conductors $\gamma \approx 0$; as we have seen in Section 1. With these assumptions the integral in (4.51) can be evaluated exactly and turns out to be:

$$\kappa^1 = \frac{3}{8} \frac{\alpha_0 \hbar}{\pi z_0^5} \left[\frac{\eta^2}{(2-\eta^2)} - \frac{2\eta^2}{(2-\eta^2)^2} \log \frac{2}{\eta^2} + 1 \right] \equiv \frac{3}{8} \frac{\alpha_0 \hbar}{\pi z_0^5} C(\eta) \tag{4.52}$$

where $C(\eta)$ stands for the expression in the square brackets. Assuming

that v is the initial velocity of the molecule, the distance travelled by it during the time t is:

$$d(t) = \frac{mv}{\kappa'}\left\{1 - \exp\left[-\frac{\kappa}{m}t\right]\right\} \quad , \tag{4.53}$$

where m is the mass of the molecule. The characteristic distance is therefore $d_\infty = \frac{mv}{\kappa'}$, which we shall evaluate for the example of Al as the substrate, and a molecule of ammonia, NH_3. The static polarizability of NH_3 is $\alpha_0 = 2.3$ Å^3 which is equivalent to 15.54 a.u. Since for Al $\omega_p = 0.565$ a.u. and, typically, $\omega_0 = 0.7$ a.u., we can take $\eta^2 \approx 0.65$. Let the velocity v be equivalent to the thermal energy at $T = 273^oK$, i.e. $v = \sqrt{2kT/m}$ (two-dimensional gas). With these data we obtain:

$$d_\infty = \frac{mv}{\kappa'} = \frac{16\pi\sqrt{2kTm}}{3\alpha_0\hbar} \times z_0^5 \approx 8z_0^5 \quad \ldots \tag{4.54}$$

This yields for $z_0 = 4$ a.u. (2 Å): $d_\infty = 2027$ a.u., or around 1000 Å. On lowering the temperature to, say, 74^oK, which is roughly the critical temperature of the adsorbed 2-D gas of NH_3, we have $d_\infty = 500$ Å.

It seems, therefore, that frictional effects on the properties of adsorbed monolayers should not be important except at very low temperatures and densities. At any rate, the frictional force would add to the phenomenon of localized adsorption, and it would be difficult to distinguish its impact from the influence of other mechanisms responsible for the localization of adsorbate molecules.

In the event that the substrate is a simple dielectric described by a permittivity

$$\varepsilon^B(i\xi) = 1 + \frac{\omega_p^2}{\omega_1^2 + \xi^2} \quad , \tag{4.55}$$

where ω_1 is a typical absorption frequency; the result (4.52) is modified slightly to

$$\kappa^1 = \frac{3}{8}\frac{\alpha_0 \hbar}{\pi z_0^5} C(\eta_1) \tag{4.56}$$

where $\eta_1^2 = (\omega_p^2 + 2\omega_1^2)/\omega_0^2$. Instead of a single molecule we now consider a semi-infinite dilute dielectric A whose permittivity is related to the polarizability $\alpha(\omega)$ of the constituent molecules by

$$\varepsilon^A(\omega) = 1 + 4\pi N\alpha(\omega) \tag{4.57}$$

where N is the density number. We can find the frictional force per unit area by integrating the forces acting on individual molecules:

$$F_x/\text{unit area} = -Nv\int_{\ell}^{\infty} \kappa^1(z_0)dz = -\frac{3}{32}\frac{\hbar v}{\pi}\frac{\varepsilon^B(0)-1}{\varepsilon^B(0)+1}\frac{N\alpha_0}{\ell^4} C(\eta_1) \tag{4.58}$$

where ℓ is the distance between A and B. Since $\varepsilon^A(0)$ is close to 1 we can write:

$$\frac{\varepsilon^A(0)-1}{\varepsilon^A(0)+1} \approx 2\pi N\alpha_0 \tag{4.59}$$

and hence eq (4.58) follows as

$$F_x/\text{unit area} = -\frac{3}{64}\frac{\hbar}{\pi^2}\frac{v}{\ell^4}\frac{\varepsilon^B(0)-1}{\varepsilon^A(0)+1}\frac{\varepsilon^A(0)-1}{\varepsilon^B(0)+1} C(\eta_1) \quad . \tag{4.60}$$

Teodorovich's result [1] for the frictional force between A and B is the same as (4.60) except for the factor $C(\eta_1)$. The reasons for the difference between our result and that of Teodorovich may be connected with inapplicability of the pair summation of the frictional van der Waals forces in our case. We should emphasize, however, that whilst

eq (4.60) may not be the best for calculating the force between two dielectric, eq (4.56) for the frictional coefficient of a single molecule is exact.

Finally let us consider the case when the zero-frequency term in the sum (4.42) is dominant. From (4.44) we can calculate $W_x(v,0)$ directly using for $S(k,\omega)$ eq (4.21) and introducing the variables u and y as in eq (4.23):

$$W_x(v,0) = \frac{\alpha_0}{\pi i} \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} du\, u\sqrt{u^2+y^2}\, \exp\left(-\frac{2z_0}{v}\sqrt{u^2+y^2}\right) \frac{\omega_s^2}{\omega_s^2 - i\gamma u - u^2} . \quad (4.61)$$

In the limit $\gamma \to 0$ we obtain (cf. eq (4.26)):

$$W_x(v,0) = \frac{\alpha_0 \omega_s^4}{2\pi v^2} \left\{ 3K_0\left(\frac{2z_0\omega_s}{v}\right) + K_2\left(\frac{2z_0\omega_s}{v}\right) \right\} . \quad (4.62)$$

It turns out, however, that for a typical example of $T = 1000^{\circ}K$ and a corresponding velocity $v = \sqrt{2kT/m}$ the frictional force is negligible for all significant distances z_0.

In this chapter we have calculated the frictional van der Waals force for a molecule travelling parallel to a vacuum-metal or a vacuum-dielectric interface. Numerical estimates show that the force is small enough to be neglected in many practical applications.

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APPENDIX

We collect and derive here some of well-known formulae concerning periodically time-dependent electromagnetic fields in dissipative media [9].

Consider a vector function:

$$\underline{F}_0(\underline{R},t) = \sum_{j=1}^{3} a_j(\underline{R})\underline{e}_j \cdot \cos(\omega t+\phi_j(\underline{R})) \tag{A4.1}$$

where $\underline{e}_j$ are basis vectors of a coordinate system. In electromagnetic problems one often has to deal with vector functions of the above form. $\underline{F}_0$ can stand for an electric or magnetic field, or a dipole moment. The function $\underline{F}_0(\underline{R},t)$ can be represented as

$$\underline{F}_0(\underline{R},t) = \mathrm{Re}\underline{F}e^{-i\omega t} \tag{A4.2}$$

with $\underline{F}$ a suitable complex vector independent of t.

Consider now two vector functions:

$$\underline{F}_0(\underline{R},t) = \mathrm{Re}\underline{F}(\underline{R})e^{-i\omega t} \quad \text{and} \quad \underline{G}_0(\underline{R},t) = \mathrm{Re}\underline{G}(\underline{R})e^{-i\omega t}$$

and calculate the average of their product during the time $T = 2\pi/\omega$. The following applies whether the product is scalar, vector or dyadic. Introducing the real and imaginary parts of vectors $\underline{F}$ and $\underline{G}$ we obtain:

$$\langle \underline{F}\,\underline{G} \rangle_T \equiv \frac{1}{T}\int_0^T (\underline{F}_r\cos\omega t + \underline{F}_i\sin\omega t)(\underline{G}_r\cos\omega t + \underline{G}_i\sin\omega t)dt \tag{A4.3}$$

$$= \frac{1}{2}(\underline{F}_r\,\underline{G}_r + \underline{F}_i\,\underline{G}_i) = \frac{1}{2}\,\mathrm{Re}\,\underline{F}\,\underline{G}^* \quad .$$

For example, if $\underline{F}_0$ stands for a dipole moment $\underline{p}_0(t) = \mathrm{Re}\underline{p}e^{-i\omega t}$ and $\underline{G}_0$ for an electric field $\underline{E}_0(t) = \mathrm{Re}\underline{E}(\omega)e^{-i\omega t}$, we can write the expression for the average potential energy of the dipole in the electric field as

$$U = -\frac{1}{2}\,\mathrm{Re}\underline{p}\cdot\underline{E}^* \quad . \tag{A4.4}$$

Suppose now that the medium is characterized by its dielectric permittivity $\varepsilon(\omega)$. Introducing the real and imaginary parts of ε: ε' and ε'', respectively, we can show that the average energy dissipated per unit time and volume to the dielectric is given:

$$\frac{d\varepsilon}{dt} = -\frac{\omega}{16\pi}\,\underline{E}^*\cdot(\varepsilon''(\omega)\underline{E}) = -\frac{\omega}{16\pi}\,\varepsilon''(\omega)\left|\underline{E}(\omega)\right|^2 \quad . \tag{A4.5}$$

Often $\varepsilon''(\omega)$ can be expressed as a combination of terms:

$$\varepsilon'' = \frac{C\gamma\omega/\omega_0}{\left(1-\frac{\omega^2}{\omega_0^2}\right)+\left(\gamma\,\frac{\omega}{\omega_0}\right)^2} \tag{A4.6}$$

where ω_0 is an absorption frequency of the medium. If the total electric field is a superposition of periodically varying fields whose frequencies lie near ω_0, the total power loss is:

$$\frac{d\varepsilon}{dt} = \int_{\omega_0-\Delta}^{\omega_0+\Delta} \frac{\omega'}{16\pi}\,\varepsilon''(\omega')\left|\underline{E}(\underline{R},\omega')\right|^2 d\omega' \quad . \tag{A4.7}$$

In the limit $\gamma \to 0$, i.e. when the absorption peak is very sharp and narrow, the imaginary part of the dielectric permittivity, ε'', becomes

$$\lim_{\gamma\to 0}\ \varepsilon''(\gamma,\omega_0) = C\pi\delta\left(1-\frac{\omega^2}{\omega_0^2}\right) \tag{A4.8}$$

Substituting (A4.8) into (A4.7) yields

$$\frac{d\varepsilon}{dt} = \frac{\omega_0^2}{32} C \left| \underline{E}(\omega_0) \right|^2 \quad . \tag{A4.9}$$

CHAPTER 5

ON SOLVENT EFFECTS IN LUMINESCENCE EMISSION

5.1 Background

Luminescence is the term describing the transition from an excited state to the ground state of a quantum system during which the radiation of a photon (photons) occurs. One distinguishes several types of luminescence, e.g. thermoluminescence, phosphorescence, fluorescence. In the case when the quantum system is a molecule the luminescence is classified depending on the total spin of the excited state; when s=0 one talks about fluorescence, and when s=1 the corresponding radiative transition is called phosphorescence [1]. The transition from the triplet excited state (i.e. when s=1) is approximately forbidden, since the ground state spin is s=0. Therefore the lifetime of the phosphorescent excited state is a few orders of magnitude longer than for fluorescence [1]. In addition to emitting a photon, the luminescent state of the molecule can decay in a radiationless manner. A full quantum-mechanical description of the phenomenon is rather complicated, especially when the molecule is embedded in a solvent as it is, for example, in the case of organic pigments occurring in living organisms.

Solvent effects on luminescence properties of solute molecules are pronounced. Firstly, one observes the shift in the emission wavelength depending on the kind of solvent [1]. Secondly, the observed lifetime of luminescence, i.e. the half-time of the radiation decay, depends very drastically on the solvent characteristics [1]. The first effect has been treated theoretically extensively [2-5], but the second is much more involved and the theories refer to specific cases [1,6]. The theoretical expressions for the "natural" lifetime of luminescence, on

the other hand, must resort to the experimental data on absorption spectra in the same solvent [1]. By "natural" lifetime one defines the inverse of the rate constant for the *radiative* decay of the excited state [1]. It is different from the observed lifetime, because the latter takes into account the radiationless processes as well.

In this Chapter we derive a semiclassical expression for the natural lifetime of luminescence in solutions. Usually, one assumes that the natural lifetime does not depend very much on the solvent properties [1,7], hence one attributes the drastic changes in the observed lifetime to the quenching processes only. We show that this is not necessarily the case; in fact, in the example considered later we show that neglect of the absorption by water can lead to an overestimate of the lifetime of a factor of 2.

A semiclassical approach to the luminescence phenomenon has recently been adopted by a number of workers [8-11]. These works, however, refer to situations, where the molecules are in a dilute non-absorbing media, or in a vacuum. The case when molecules are in a solution has been treated by Baylis [2], McRae [3] and Robertson *et al* [4,5], where the fluorescence frequency shift has been calculated. The method of calculation is based on the reaction field concept introduced by Onsager (cf. Böttcher [12]). The fluorescent molecule is considered as a quasistatic dipole in the centre of a spherical cavity created in the solvent. The field inside the cavity is the sum of the direct dipole field plus the reaction field due to the polarization induced in the dielectric surround. This reaction field acts on the oscillating dipole, thus reducing its oscillation frequency.

It appears that the considerations based on the quasistatic approximation are oversimplified. In particular, the rate of the energy

radiation through the cavity walls cannot be calculated in this approximation, and hence the fluorescence natural lifetime has to be assumed from outside the model. In this Chapter we consider the exact electromagnetic problem of radiation from the molecule to the solvent.

5.2 Linear oscillator model for luminescent molecule

In a semi-classical approach one treats the luminescence as a process of radiation of a classical electric dipole which arises out of the oscillating motion of elastically bound electrons [8]. The equation of motion of one electron is:

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = -\frac{e}{m} E \qquad (5.1)$$

where x is the position of the electron with respect to its equilibrium position, γ is the damping factor describing radiative and radiationless loss of the energy of the oscillator, ω_0 is the frequency of luminescent light in a vacuum, and E is a certain external electric field. The dipole moment associated with the oscillating electron is: $\mu = -ex$, hence eq (5.1) can also be written in the form involving the dipole moment [8]:

$$\ddot{\mu} + \gamma\dot{\mu} + \omega_0^2\mu = \frac{e^2}{m} E \qquad (5.1a)$$

In the present case the electric field E is the field due to the dipole itself (excluding the free space field), thus we can assume that E is proportional to μ. Admitting complex functions in eq (5.1a) we can write:

$$E = T\mu \qquad (5.2)$$

where T (complex number) depends on the particular geometry of the

problem. Substituting (5.2) into (5.4), and seeking solutions to the latter in the form $\mu = \mu_0 e^{-i\Omega t}$ we obtain:

$$-\Omega^2 - i\gamma\Omega + \omega_0^2 - \frac{e^2}{m}T = 0 \quad . \tag{5.3}$$

From eq (5.3) the solution Ω follows as:

$$\Omega = -\frac{i\gamma}{2} + \sqrt{\omega_0^2 - \frac{e^2}{m}T - \frac{\gamma^2}{4}} \quad . \tag{5.4}$$

Assuming that both $\frac{e^2}{m}T$ and $\gamma^2/4$ are small compared with ω_0^2 we can expand the square root in eq (5.4) to obtain:

$$\Omega = -\frac{i\gamma}{2} + \omega_0 - \frac{\gamma^2}{8\omega_0} - \frac{1}{2}\frac{e^2}{m}\frac{T}{\omega_0} \quad . \tag{5.5}$$

We now proceed to calculate the average energy loss of the dipole. The instantaneous mechanical energy of the electron is:

$$E = \frac{m\dot{x}^2}{2} + \omega_0^2 m x^2 \equiv \frac{m}{2e^2}(\dot{\mu}_r^2 + \omega_0^2 \mu_r^2) \tag{5.6}$$

where $\mu_r = \mathrm{Re}\mu_0 e^{-i\Omega t}$. The energy loss is therefore

$$\frac{dE}{dt} = \frac{m}{e^2}(\dot{\mu}_r\ddot{\mu}_r + \omega_0^2 \mu_r \dot{\mu}_r) = -\frac{m}{e^2}\gamma\dot{\mu}_r + E_r\dot{\mu}_r \tag{5.7}$$

where $E_r = \mathrm{Re}E$, and the last step follows from eq (5.1a).

We limit ourselves to consideration of the cases in which the real part of Ω, $\mathrm{Re}\Omega \equiv \Omega_r$ is much larger than its imaginary part: $\mathrm{Im}\Omega \equiv \Omega_i$. Under these circumstances we can calculate the average energy loss per period $t_p = 2\pi/\Omega_r$. According to eq (A4.3) from the Appendix to Chapter 4, and from eq (5.7) we have:

$$\overline{\frac{dE}{dt}} = -\frac{1}{2}\frac{m}{e^2}\gamma \mathrm{Re}(\dot{\mu}\dot{\mu}^*) + \frac{1}{2}\mathrm{Re}(E\mu^*) \quad , \tag{5.8}$$

where the bar on the l.h.s. denotes the average. Because $\mu = \mu_0 e^{-i\Omega t}$ and $E = T\mu$ we obtain:

$$\begin{aligned} \overline{\frac{dE}{dt}} &= e^{2\Omega_i t}\left(-\frac{\gamma m}{2e^2}|\Omega\mu_0|^2 + \frac{1}{2}\mathrm{Re}iT\Omega^*|\mu_0|^2\right) \\ &= |\Omega\mu_0|^2 e^{2\Omega_i t}\left(-\frac{\gamma m}{2e^2} + \frac{1}{2}\mathrm{Re}\frac{iT}{\Omega}\right) \quad . \end{aligned} \tag{5.9}$$

On the other hand, from eq (5.5) we obtain for the imaginary part of the frequency:

$$\Omega_i = -\frac{\gamma}{2} - \frac{1}{2}\frac{e^2}{m}\frac{\mathrm{Im}T}{\omega_0} \quad . \tag{5.10}$$

Combining eqs (5.10) and (5.9) and taking into account the fact that $|\frac{\Omega_i}{\Omega}| << 1$ we obtain:

$$\overline{\frac{dE}{dt}} = \frac{m}{e^2}|\Omega\mu_0|^2\Omega_i e^{2\Omega_i t} \quad . \tag{5.11}$$

We now proceed with the calculation of the energy loss rate by solving the following electromagnetic problem.

5.3 Electric dipole radiation from a cavity

This electromagnetic problem is readily solvable by using the Hertz-Debye potential technique, well-known in the scattering theory [13,14]. The geometry of the problem is displayed in Fig. 5.1. The inside of the dielectric sphere is filled with a non absorbing dielectric characterized by the permittivity ε_1, whilst the outside is a homogeneous medium of complex permittivity $\varepsilon_2 = n_2^2 - \kappa_2^2 + 2in_2\kappa_2$, where n_2 and κ_2 are real and imaginary parts of the complex refractive index $m_2 = n_2 + i\kappa_2$. The

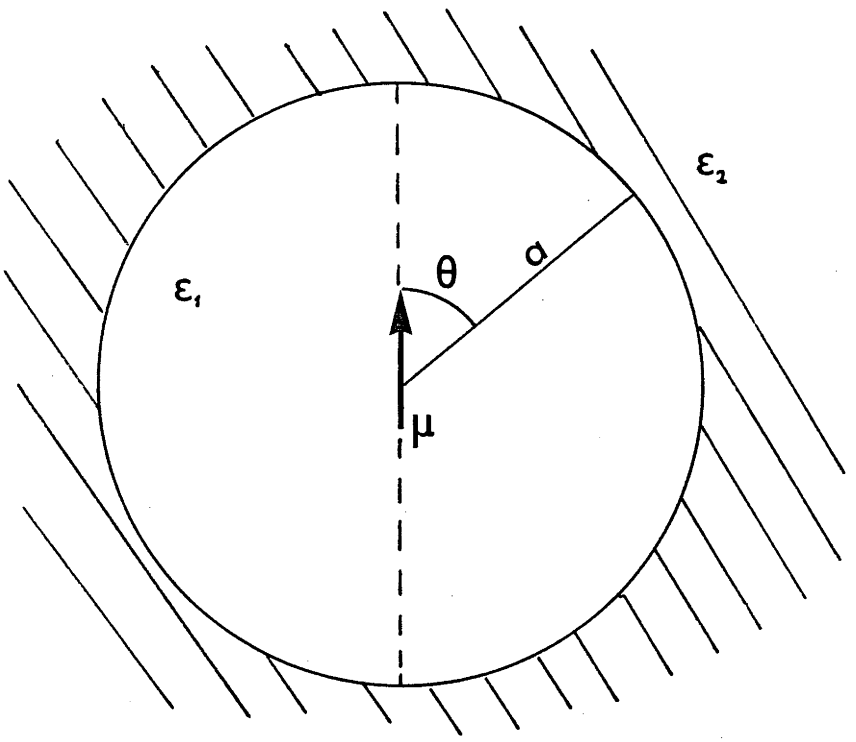

Fig. 5.1. The dipole μ is located in the centre of a cavity characterized by ε_1, which is embedded in an absorbing dielectric of ε_2.

dipole is located in the centre of the cavity. We introduce the polar coordinate system (r,θ,ϕ), so that $r=0$ is the position of the dipole and $\theta=0$ is its direction. The dipole oscillates with a (complex) frequency Ω, i.e. $\mu = \mu_0 e^{-i\Omega t}$.

The problem is to find the solution to Maxwell's equations:

$$\begin{aligned} \text{curl } \underline{H}^j &= -\frac{i\Omega}{c}\varepsilon_j \underline{E}^j \\ \text{curl } \underline{E}^j &= \frac{i\Omega}{c}\underline{H}^j \end{aligned} \qquad j = 1,2 \qquad (5.12)$$

with the boundary conditions of the continuity for tangential components:

$$\underline{E}^1_{tang} = \underline{E}^2_{tang} , \quad \underline{H}^1_{tang} = \underline{H}^2_{tang} \quad \text{for} \quad r = a$$

where a is the radius of the sphere.

Other requirements are that for $r=0$ the electromagnetic field $(\underline{E}^1, \underline{H}^1)$ should have a singularity appropriate to the electric dipole source, and for $r >> a$ and $r >> \lambda_2$, where $\lambda_2 = \frac{2\pi c}{|m_2|\Omega_r}$, the field should have a radiation pattern of an effective dipolar source.

We introduce [13] the Hertz-Debye scalar potentials ${}^{e}\Pi^{j}$ and ${}^{m}\Pi^{j}$. They satisfy the Helmholtz equation:

$$\underline{\nabla}^2 \, {}^{e}\Pi^{j} + k_j \, {}^{e}\Pi^{j} = 0 , \quad j = 1,2 \tag{5.13}$$

where

$$k_j = \frac{\Omega}{c} m_j .$$

The Hertz-Debye potentials are related to the electromagnetic field through the equations [13]:

$$\text{a)} \quad E_r^j = \frac{\partial^2 (r\,{}^{e}\Pi^{j})}{\partial r^2} + k_j^2 r\,{}^{e}\Pi^{j}$$

$$\text{b)} \quad E_\theta^j = \frac{1}{r}\frac{\partial^2 (r\,{}^{e}\Pi^{j})}{\partial r \partial \theta} + \frac{\Omega}{c}\frac{1}{r\sin\theta}\frac{\partial (r\,{}^{m}\Pi^{j})}{\partial \phi}$$

$$\text{c)} \quad E_\phi^j = \frac{1}{r\sin\theta}\frac{\partial^2 (r\,{}^{e}\Pi^{j})}{\partial r \partial \phi} - \frac{\Omega}{c}\frac{1}{r}\frac{\partial (r\,{}^{m}\Pi^{j})}{\partial \theta} \tag{5.14}$$

$$\text{d)} \quad H_r^j = k_j^2 r\,{}^{m}\Pi^{j} + \frac{\partial^2 (r\,{}^{m}\Pi^{j})}{\partial r^2}$$

$$\text{e)} \quad H_\theta^j = -\frac{i\Omega}{c}\varepsilon_j \frac{1}{r\sin\theta}\frac{\partial (r\,{}^{e}\Pi^{j})}{\partial \phi} + \frac{1}{r}\frac{\partial^2 (r\,{}^{m}\Pi^{j})}{\partial r \partial \theta}$$

$$\text{f)} \quad H_\phi = \frac{i\Omega}{c}\varepsilon_j \frac{1}{r}\frac{\partial (r\,{}^{e}\Pi^{j})}{\partial \theta} + \frac{1}{r\sin\theta}\frac{\partial^2 (r\,{}^{m}\Pi^{j})}{\partial r \partial \phi}$$

Now the continuity conditions for tangential components of $\underline{E}$ and $\underline{H}$ at the surface of the cavity $r=a$ can be translated into the language of the Hertz-Debye potentials as follows [13]:

$$\begin{aligned}
&\text{a)} \quad \left.\frac{\partial(r\,{}^{e}\Pi^{1})}{\partial r}\right|_{r=a} = \left.\frac{\partial(r\,{}^{e}\Pi^{2})}{\partial r}\right|_{r=a} \\
&\text{b)} \quad \left.\varepsilon_1\,{}^{e}\Pi^{1}\right|_{r=a} = \left.\varepsilon_2\,{}^{e}\Pi^{2}\right|_{r=a} \\
&\text{c)} \quad \left.\frac{\partial(r\,{}^{m}\Pi^{1})}{\partial r}\right|_{r=a} = \left.\frac{\partial(r\,{}^{m}\Pi^{2})}{\partial r}\right|_{r=a} \\
&\text{d)} \quad \left.{}^{m}\Pi^{1}\right|_{r=a} = \left.{}^{m}\Pi^{2}\right|_{r=a}
\end{aligned} \tag{5.15}$$

Imagine a homogenous medium of the dielectric permittivity ε and refractive index $m^2 = \varepsilon$. A dipolar source $p = p_0 e^{-i\Omega t}$ embedded in this medium produces the field whose components are [13]:

$$\begin{aligned}
&\text{a)} \quad E_r = \frac{2}{\varepsilon} p_0 e^{-i\Omega t} e^{ikr}\left[\frac{1}{r^3} - \frac{ik}{r^2}\right]\cos\theta \\
&\text{b)} \quad E_\theta = \frac{1}{\varepsilon} p_0 e^{-i\Omega t} e^{ikr}\left[\frac{1}{r^3} - \frac{ik}{r^2} - \frac{k^2}{r}\right]\sin\theta \\
&\text{c)} \quad H_\phi = \frac{m}{\varepsilon} p_0 e^{-i\Omega t} e^{ikr}\left[-\frac{ik}{r^2} - \frac{k^2}{r}\right]\sin\theta \\
&\text{d)} \quad E_\phi = H_\theta = H_r = 0 \,.
\end{aligned} \tag{5.16}$$

where we have omitted the time factor: $e^{-i\Omega t}$.

This field can be obtained using eqs (5.14) from the electric potential:

$${}^{e}\Pi = -\frac{p_0}{\varepsilon}\frac{ike^{ikr}}{r}\left[1 - \frac{1}{ikr}\right]\cos\theta \,. \tag{5.17}$$

We shall try, therefore, to represent the solution to the problem under

consideration in terms of the potentials:

$$\text{a)} \quad {}^{e}\Pi^{2} = -\frac{A}{\varepsilon_1}\frac{ik_2 e^{ik_2 r}}{r}\left[1 - \frac{1}{ikr}\right]\cos\theta \qquad (r \geqslant a)$$

$$\text{b)} \quad {}^{m}\Pi^{2} = 0$$

(5.18)

$$\text{c)} \quad {}^{e}\Pi^{1} = -\frac{\mu_0}{\varepsilon_1}\frac{ik_1 e^{ik_1 r}}{r}\left[1 - \frac{1}{ik_1 r}\right]\cos\theta + \Pi_r^1 \qquad (r \leqslant a)$$

$$\text{d)} \quad {}^{m}\Pi^{1} = 0 \ .$$

The unknown quantities are the constant A and the potential Π_r^1 describing the reaction field in the cavity.

It is known [13] that the solution to the Helmholtz equation in spherical coordinates can be represented as a series involving Ricatti-Bessel functions $\psi_\ell(kr)$, $\chi_\ell(kr)$ and Legendre polynomials $P_m^\ell(\cos\theta)$. The reaction field potential Π_r^1 can be written as follows:

$$r\Pi_r^1 = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \{c_\ell \psi_\ell(k_1 r) + d_\ell \chi_\ell(k_1 r)\} P_\ell^{(m)}(\cos\theta) \times [a_m \cos(m\phi) + b_m \sin(m\phi)] \ . \qquad (5.19)$$

From eqs (5.18) and the continuity condition (5.15b) we conclude that the angular dependence of the reflected field potential must be through the factor $\cos\theta$. This leaves only one term in the series (5.19):

$$r\Pi_r^1 = c\psi_1(k_1 r) + d\chi_1(k_1 r)\cos\theta \ . \qquad (5.20)$$

The first order Ricatti-Bessel functions are explicitly:

$$\text{a)}\quad \psi_1(z) = \frac{\sin z}{z} - \cos z\ , \qquad \text{b)}\quad \chi_1(z) = \frac{\cos z}{z} + \sin z\ . \tag{5.21}$$

From eq (5.21) we see that $\chi_1(k_1 r)$ is singular at r=0; thus we must put in (5.20) d=0 since the singularity in the total potential ${}^{e}\Pi^{1}$ at r=0 has already been accounted for by the first term in the r.h.s. of eq (5.18c). Finally, we can write the total potential as:

$$r\,{}^{e}\Pi^{1} = \left\{ -\frac{\mu_0}{\varepsilon_1}\, i k_1 e^{i k_1 r}\left[1 - \frac{1}{i k_1 r}\right] + c\psi_1(k_1 r)\right\}\cos\theta\ . \tag{5.22}$$

Now the boundary conditions (5.15a,b) can be written as:

$$\frac{A}{\varepsilon_2}\, k_2^2 e^{i k_2 a}\left[1 - \frac{1}{i k_2 a} - \frac{1}{k_2^2 a^2}\right] = \frac{\mu_0}{\varepsilon_1}\, k_1^2 e^{i k_1 a}\left[1 - \frac{1}{i k_1 a} - \frac{1}{i k_1^2 a^2}\right] + c k_1 \psi_1'(k_1 a) \tag{5.23}$$

and

$$i A k_2\left[1 - \frac{1}{i k_2 a}\right] = k_1 i \mu_0 e^{i k_1 a}\left[1 - \frac{1}{i k_1 a}\right] - c\varepsilon_1 \psi_1(k_1 a) \tag{5.24}$$

where $\psi_1'(k_1 a) = \dfrac{d\psi}{d(k_1 a)} = -\dfrac{\sin k_1 a}{(k_1 a)^2} + \dfrac{\cos k_1 a}{k_1 a} + \sin k_1 a\ .$

Eliminating the constant c from eqs (5.23), (5.24), and then solving for A, we obtain:

$$A = \mu_0 \frac{[f(k_1 a)\psi_1(k_1 a) + g(k_1 a)\psi_1'(k_1 a)]}{[f(k_2 a)\psi_1(k_1 a) + \frac{k_2}{k_1} g(k_2 a)\psi_1'(k_1 a)]}\, e^{i(k_1 - k_2)a}\ . \tag{5.25}$$

In eq (5.25) we have introduced the notation:

$$\text{a)}\quad f(k_j a) = \left[1 - \frac{1}{i k_j a} - \frac{1}{(k_j a)^2}\right] \qquad j = 1,2$$

$$\text{b)}\quad g(k_j a) = i - \frac{1}{k_j a}\ . \tag{5.26}$$

In our case the cavity is of the molecular size, whilst the wavenumber corresponds to the visible or ultra-violet wavelength. We can, therefore, consider the limit $|k_j a| \ll 1$. From eqs (5.26) and (5.21a) we find:

$$\begin{aligned} &\text{a)} \quad f(k_2a)\psi_1(k_1a) + g(k_1a)\psi_1'(k_1a) \approx -1 \\ &\text{b)} \quad f(k_2a)\psi_1(k_1a) + \frac{k_2}{k_1} g(k_2a)\psi(k_1a) \approx -\frac{1}{3}\frac{\varepsilon_1}{\varepsilon_2} - \frac{2}{3} \end{aligned} \tag{5.27}$$

Upon substituting eqs (5.27) into (5.25) we obtain:

$$A \approx \mu_0 \frac{3\varepsilon_2}{2\varepsilon_2+\varepsilon_1} e^{i(k_1-k_2)a} \quad . \tag{5.28}$$

The above result is the well-known expression for the effective static dipole moment (apart from the factor $e^{i(k_1-k_2)a}$) of the cavity with the dipole μ_0 in the centre [12].

Let us now calculate the flux of energy through the cavity wall r=a. We shall need the complex Poy nting vector $\underline{S} = \frac{c}{8\pi} \underline{E} \times \underline{H}^*$. In our case, in view of the fact that $E_\phi = H_\theta = H_r = 0$ we can write:

$$(\underline{S} \cdot \underline{e}_r)\Big|_{r=a} = \frac{c}{8\pi} E_\theta H_\phi^*\Big|_{r=a} \tag{5.29}$$

where $\underline{e}_r = \frac{\underline{r}}{r}$. From eqs (5.16), specialized to the present case (i.e. having let $k = k_2$, $p_0 = A$, $\varepsilon = \varepsilon_2$), and (5.29) we obtain:

$$(\underline{S} \cdot \underline{e}_r) = \frac{c}{8\pi} \frac{k_2 |k_2|^2}{\varepsilon_2 a^2} |A|^2 \frac{\Omega}{c} e^{-2\mathrm{Im}k_2 a} h(k_2a) \sin^2\theta \; e^{+2\Omega_i t} \tag{5.30}$$

where we have reintroduced the time dependence and:

$$h(k_2a) = \left(1 - \frac{1}{ik_2a} - \frac{1}{k_2^2a^2}\right)\left(1 + \frac{1}{ik_2^*a}\right) . \tag{5.31}$$

The average power loss can be expressed through the Poy nting vector as:

$$\overline{\frac{dE}{dt}}^{rad} = \int_{r=a} \mathrm{Re}(\underline{S} \cdot \underline{e}_r) d\sigma \quad . \tag{5.32}$$

Substituting into (5.32) eq (5.30) we obtain:

$$\overline{\frac{dE}{dt}}^{rad} = \frac{2}{3} \mathrm{Re} \left\{ \frac{\Omega|\Omega|^2}{c^2} |A|^2 e^{-2\mathrm{Im}k_2 a} k_2^* h(k_2 a) \right\} e^{2\Omega_i t} \quad . \tag{5.33}$$

Using equation (5.28) for A we obtain from (5.33):

$$\overline{\frac{dE}{dt}}^{rad} = \frac{2}{3} \left| \frac{3\varepsilon_2}{2\varepsilon_2+\varepsilon_1} \right|^2 \frac{|\Omega\mu_0|^2}{c^2} e^{-2\mathrm{Im}k_1 a} e^{2\Omega_i t} \mathrm{Re}[k_2^* h(k_2 a)\Omega] \quad . \tag{5.34}$$

Since $\Omega_i << \Omega_r \approx |\Omega|$ we can write:

$$\overline{\frac{dE}{dt}}^{rad} = \frac{2}{3} |\mu_0|^2 \left| \frac{3\varepsilon_2}{2\varepsilon_2+\varepsilon_1} \right|^2 \frac{|\Omega|^4}{c^3} \left[n_2 + \frac{1}{k_0 a} \frac{\kappa_2^2}{|m_2|^2} + \frac{1}{(k_0 a)^2} \frac{4n_2\kappa_2^2}{|m_2|^4} + \right. \tag{5.35}$$

$$\left. + \frac{1}{(k_0 a)^3} \frac{2\kappa_2 n_2}{|m_2|^4} \right] e^{2\Omega_i t}$$

where the last factor follows from calculating the real parts of $k_2^* h(k_2 a)$ from eq (5.31). We have also used the notation: $k_0 = \frac{|\Omega|}{c}$, so that $k_2 = k_0 m_2$.

5.4 The lifetime of luminescence

We proceed with application of the results of the two preceding sections in calculating the luminescence lifetime of molecules in solutions. The energy loss rate (5.11) is the total loss due to both radiative and radiationless relaxation. The characteristic lifetime associated with this is $\tau = 1/\Omega_i$, and this is the observed experimentally decay time of luminescence. On the other hand the energy loss described by eq (5.35)

is due to the radiation only. The characteristic lifetime associated with the radiation is the natural lifetime τ_0.

The lifetimes are related through the equation [1]:

$$\bar{\tau} = q\tau_0 \tag{5.36}$$

where q is the probability of the radiative transition from the excited to ground state (luminescence quantum efficiency). We can write, therefore:

$$\overline{\frac{dE}{dt}} = \frac{1}{q}\overline{\frac{dE}{dt}}^{rad} . \tag{5.37}$$

Hence and from eqs (5.36), (5.35) and (5.11) we obtain:

$$(\tau_0)^{-1} \equiv q\Omega_i = \frac{2}{3}\frac{e^2}{m}\left|\frac{3\varepsilon_2}{2\varepsilon_2+\varepsilon_1}\right|^2 \frac{|\Omega^2|}{c^3} \times\left[n_2 + \frac{\kappa_2^2}{(k_0a)|m_2|^2} + \frac{4n_2\kappa_2^2}{(k_0a)^2|m_2|^4} + \frac{2\kappa_2 n_2}{(k_0a)^3|m_2|^4}\right] . \tag{5.38}$$

The above equation can be approximated by:

$$(\tau_0)^{-1} \approx \frac{2}{3}\frac{e^2}{m}\frac{|\Omega|^2}{c^3}\frac{9n_2^4}{(2n_2^2+n_1^2)^2} \times \left[n_2 + \frac{2\kappa_2}{(k_0a)^3 n_2^3}\right] \tag{5.39}$$

because the second and last terms in the square bracket in eq (5.38) are usually much smaller than the other two. Also, we have put $|m_2|^4 \approx n_2^4$ and $\varepsilon_2 \approx n_2^2$, $\varepsilon_1 = n_1^2$, because the effect of the imaginary part of ε_2 has only a small effect on the factors: $|3\varepsilon_2|/|2\varepsilon_2+\varepsilon_1|$ and $1/|m_2|^4$.

To estimate the effect of absorption coefficient, κ_2, on the natural luminescence lifetime, consider a fluorescent atom of Eu in water solution. The emission wavelength is 6180 Å [6] and the

extinction coefficient of water at this wavelength is $k_{ext} \equiv \frac{4\pi}{\lambda} \kappa_2 =$ 0.00258 [15].

Hence it follows that:

$$\frac{2\kappa_2}{(k_0 a)^3 n_2^3} \approx \frac{24.1}{a^3 n_2^3} \text{Å}^3$$

where a is the cavity radius in Ångstroms. Assuming, typically, $a = 2$Å we find that the second term in the square brackets on the r.h.s. of eq (5.39) is approximately 1.2, whereas the first one, which is the refractive index of water, is 1.33. If we neglected the absorption of light by water, the result for the lifetime would be 2 times greater. This example provides an argument that the absorption properties of the solution can have profound effects on the luminescence natural lifetimes.

As we have mentioned in the first section to this Chapter, the quantity τ_0 can also be calculated using an adaptation of the well-known Einstein's result [1]. This expression, however, requires the knowledge of the absorption spectrum of the solute in the same solution. To our knowledge, eq (5.39) is the first attempt to calculate the effect of solvent on the fluorescent radiative lifetime without reference to the absorption spectra.

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CHAPTER 6

THE THEORY OF THE ORIGIN OF THE 520 nm DIFFERENCE ABSORPTION BAND OF CHLOROPLASTS

6.1 Introduction

In plant cells the conversion of light to chemical energy takes place in organelles called chloroplasts, which are about 5-10 μ in size [1]. Inside the chloroplasts the photosynthetic membranes (thylakoids) are usually arranged in stacks termed grana. The grana are particles of about 0.5 μ in size [1]. Apart from the grana the chloroplast contains a fraction of unstacked membranes (stroma), but since most of the photosynthetic pigment is inside the grana we can assume that the environment of grana is the cytoplasmic fluid only, as far as optical properties of chloroplasts are concerned.

The main photosynthetic pigments are chlorophyll a and b [1]. They absorb in the blue and red parts of the visible spectrum. In addition to chlorophylls there are numerous accessory pigments absorbing throughout the whole visible range. The role of these pigments in the photosynthetic process can be studied by difference spectroscopy.

Difference absorption spectra are obtained by comparing the absorbancies of weak monochromatic beams of varying wavelength passing through a chloroplast suspension in darkness (that is, when all processes of photosynthesis are stopped), with the analogous measurements in the case when the sample has been illuminated by strong actinic light. The difference spectra exhibit characteristic maxima and minima which are indicative of photopigment activities in the chloroplasts. Yet the peak in the region of 520 nm wavelength cannot be attributed to a specific photopigment of the chloroplasts, and recently [2] the suggestion was made

that the light-induced changes in absorbancy in this region might be due to the selective dispersion of the refractive index caused by the absorption band of the carotenoids.

Apart from initiating series of chemical reactions in the chloroplast membranes, light also induces conformational changes which can be monitored by electron microscopy. In particular, a shrinkage of the thylakoid grana structure of the chloroplasts upon actinic illumination has been demonstrated [3]. Changes in light scattering and absorption caused by the conformational changes have long been known and have attracted some theoretical attention [4]. However, difference spectra have not been theoretically discussed and the origin of the 520 nm peaks has remained obscure. This is somewhat surprising as this band is important since it is indicative of the establishment of the high energy state of the energy transducing photosynthetic mechanism of the chloroplasts.

In the present chapter we present the results of a theoretical analysis based on a model of light-induced optical-conformational changes in the stacked thylakoids (grana) of the chloroplasts. On the basis of a simplified model structure we calculate the effective refractive index of the grana. This is a function of the incident wavelength of the light and the assumed geometrical parameters of the grana stacks. The light induced hydrogen ion, H^+, uptake by the chloroplast grana is accompanied by an efflux of Mg ions and water which leads to a shrinking or flattening of the thylakoid layers. We assumed that the grana formations of the chloroplasts were sufficiently large to apply the corrected van de Hulst equation [5] to calculate the extinction cross-sections in both light and dark conditions. This theoretical approach shows that the model system of grana gives a maximum of the light minus dark difference spectrum in the region of 520 nm. The precise wavelength at which the maximum can occur is model dependent, but lies close to 520 nm for a fairly broad

range of parameters.

In the process of the calculation, for simplicity, we have taken account of only two photopigments, chlorophyll a (438, 676) and collectively the carotenoids (500) where the absorbance peaks are given in nm. It is known that chlorophyll b is not essential to generate the 520 nm band since a barley mutant without this chlorophyll also gives similar light induced effects with the same peak [6].

6.2 Model and results

Significant progress has been achieved recently in the study of the structure of chloroplast membranes (thylakoids) and a fluid mosaic membrane model seems plausible [7]. On the basis of this and on recent information concerning chlorophyll-protein complexes, their dimensions and possible structure [8], we visualize the grana cross-sections as shown in Fig. 6.1. The circles represent the chlorophyll-protein complexes -- their sizes vary from 80 Å to 160 Å, apparently depending upon the type of the complex. These are embedded in the lipid bilayer membrane with possible partial external surface protein layer attached to the intrinsic complexes. These external proteins are not shown in Fig. 6.1. The fluid cytoplasm is located in the regions between the membranes, and these layers contract upon illumination. The refractive index of cytoplasm may rise slightly due to a loss of water. The effective refractive index of the whole structure changes then for two reasons: (1) a decrease in the volume fraction of cytoplasm in the whole granum and (2) an increase in the refractive index of cytoplasm layers. Changes in scattering and absorbancy of light follow the alterations in the refractive index.

It is well known that multilayered structures are optically anisotropic [9]. This is the reason why we need, in fact, two refractive indices to describe optical properties of grana. Denote by $m^{\perp}$ the

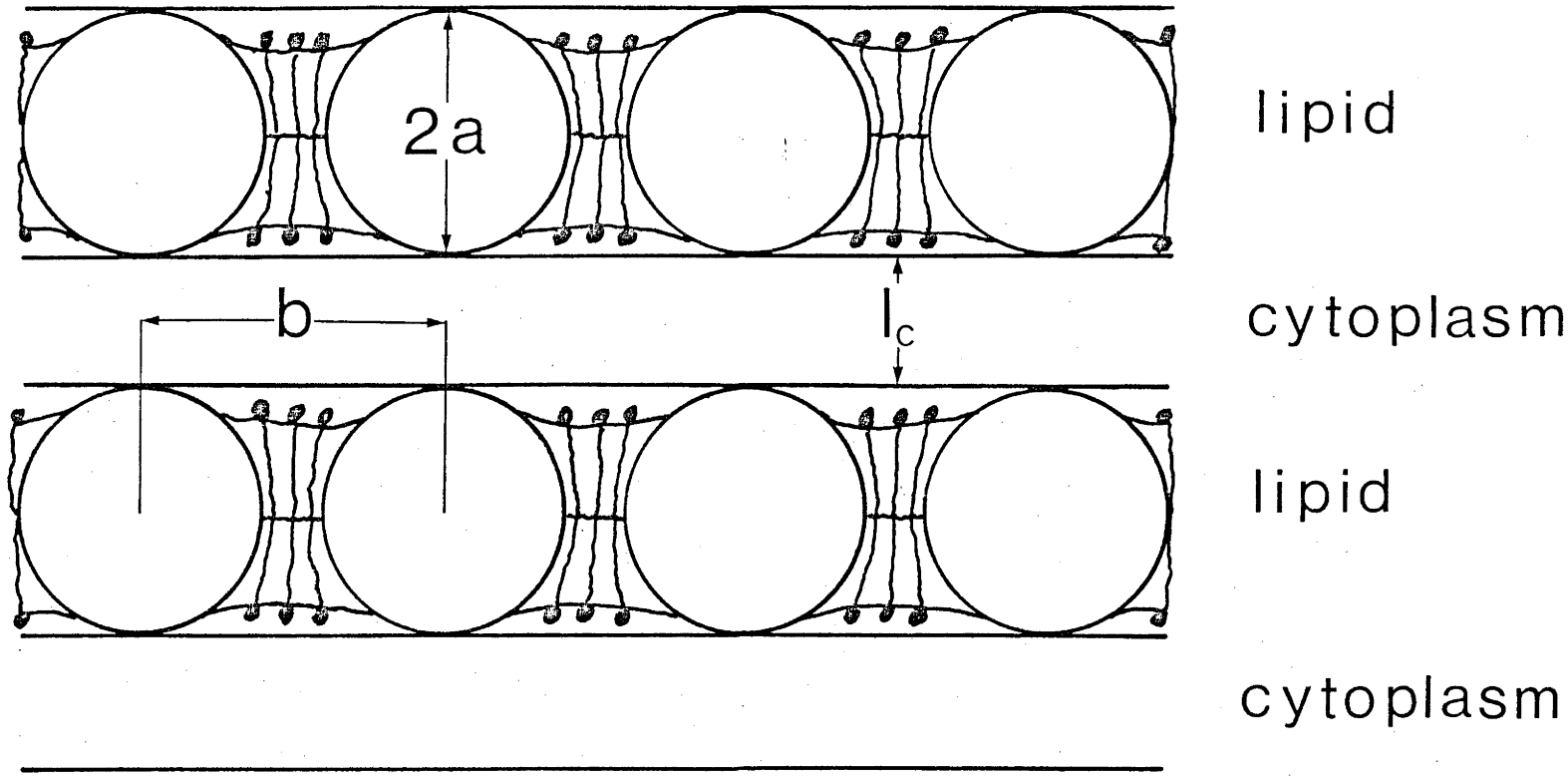

Fig. 6.1. The schematic cross-section of grana. The circles represent protein-chlorophyll complexes, a - is their radius, b - the centre-to-centre separation. The protein-chlorophyll complexes together with their lipid surround effectively represent a slab of thickness 2a. The intervening cytoplasm layers have thickness l_c, and the sandwiched membrane-cytoplasm structure repeats itself many times.

refractive index for light polarized perpendicularly to the membranes and by $m^{\parallel}$ the refractive index for light polarized parallel to them. Since the grana absorb light both the refractive indices are complex functions of the wavelength. Let $n^{\perp}$ and $n^{\parallel}$ be the real parts of $m^{\perp}$ and $m^{\parallel}$, respectively, and $-k^{\perp}$ and $-k^{\parallel}$ denote their imaginary parts. In other words, we may express $m^{\parallel}$ and $m^{\perp}$ as follows: $m^{\parallel} = n^{\parallel} - ik^{\parallel}$ and $m^{\perp} = n^{\perp} - ik^{\perp}$. We mention here that in the present case the difference between $m^{\perp}$ and $m^{\parallel}$ is small, thus Figs. 6.2 and and 6.3 refer to $m^{\perp}$ only; analogical plots for $m^{\parallel}$ would be very similar.

Fig. 6.2 shows the real part of the refractive index of grana $-n^{\perp}(\lambda)$, where λ is the wavelength, for light polarized perpendicularly to the membranes. The curve exhibits fluctuations in the values of $n^{\perp}$ around the wavelengths of peak absorptions. This phenomenon is known as selective, or anomalous, dispersion [9,10]. The calculations leading to Fig. 6.2 were based on equations derived in the next section. The geometrical parameters used in these are detailed in the caption to Fig. 6.1. We assumed that chlorophyll a is located solely in the spheres and that the carotenoids were confined to their lipid surround. According to published data [8], the protein-to-chlorophyll ratio in the spheres was taken as 13:7, whilst the carotenoids comprised 4.5% of the remaining lipid mass, i.e. excluding chlorophyll. The absorption bands were centred around 438 nm and 676 nm for chlorophyll a, and 495-500 nm for the carotenoids in vivo.

For the light-induced state the only change made was to reduce the thickness of the cytoplasm layers from 30 Å to 15 Å. The membrane thickness was left unchanged and the volume of a granum stack decreased by 13.6%. In Fig. 6.3 we plot the light minus dark difference in the refractive index $n^{\perp}$ as a function of wavelength. It is seen from this figure that the increase is not uniform, but fluctuates around the

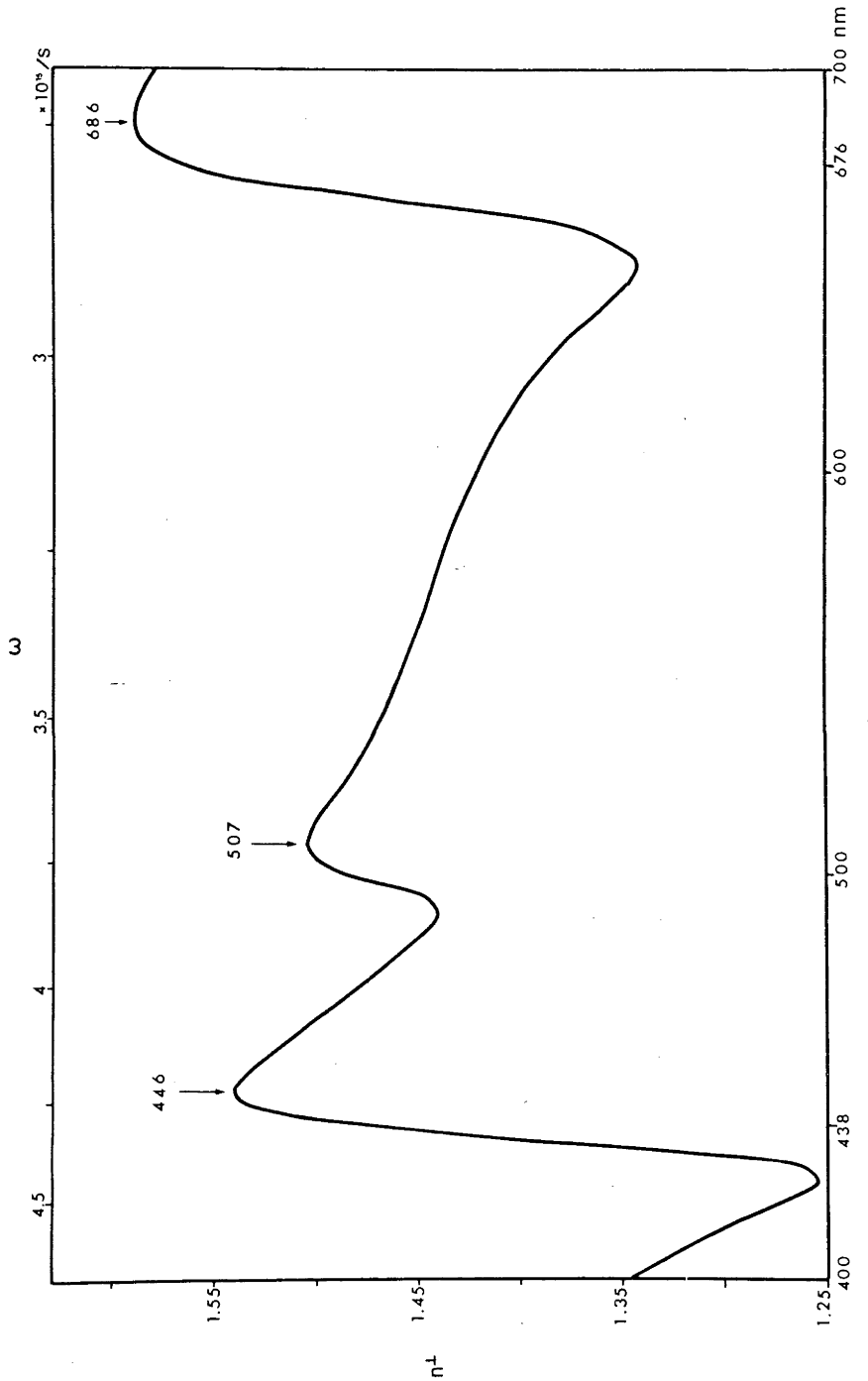

Fig. 6.2. The refractive index of dark adapted grana for light polarized perpendicularly to the membranes versus the wavelength of light.

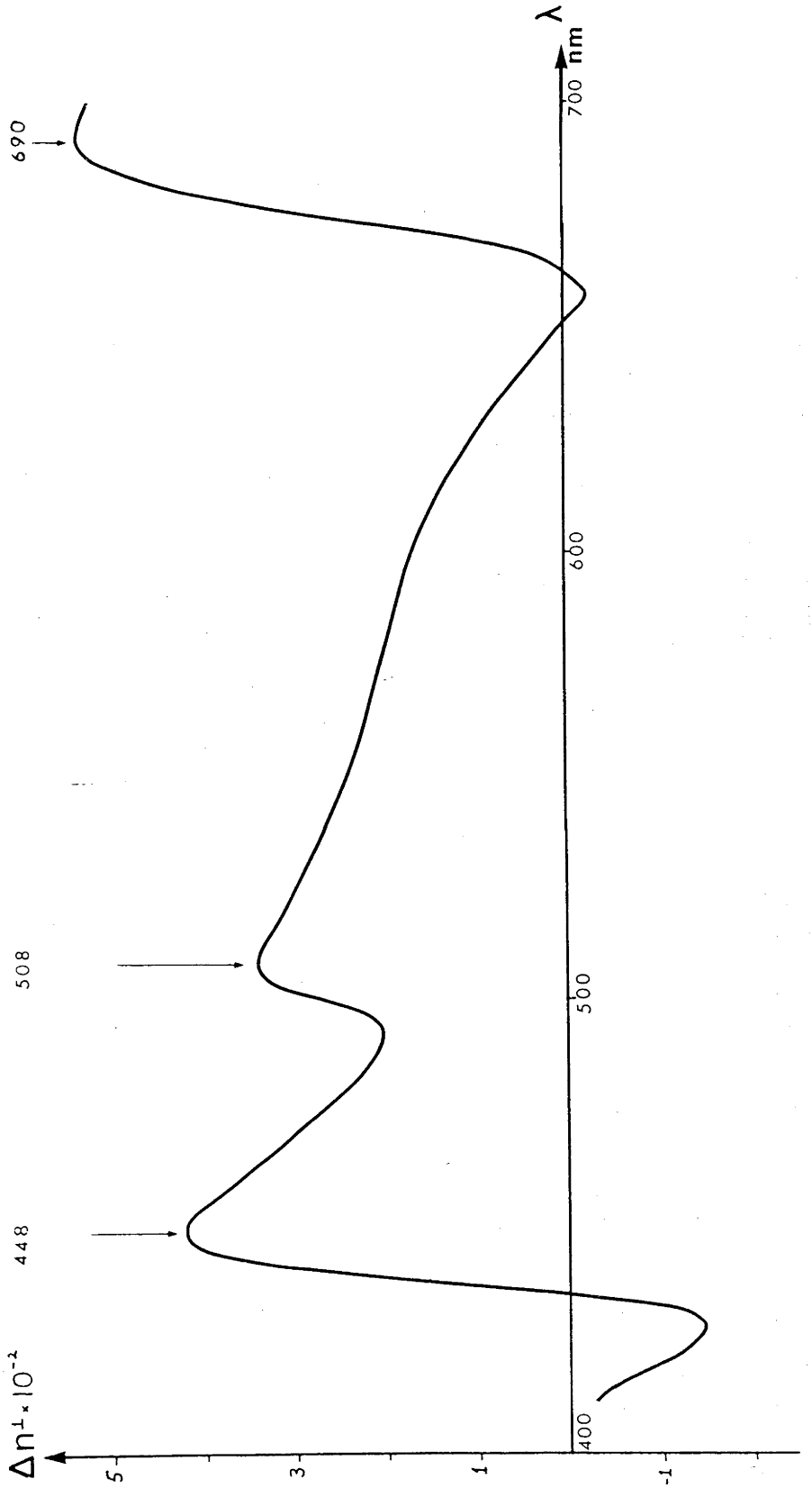

Fig. 6.3. The light minus dark difference in the refractive index $n^{\perp}(\lambda)$ versus the wavelength of light.

absorption wavelengths in the same manner as does the refractive index (Fig. 6.2).

For absorbancy calculations a granum structure was assumed to be equivalent to a spherical particle of the mean refractive index $m' = (m^{\perp} + 2m^{\parallel})/3$. The particle was immersed in a medium of the refractive index $n_0 = 1.34$, which corresponds to a 0.33 M solution of sorbitol as used in measurements on chloroplasts. Extinction cross-sections, which are proportional to measured absorbancies, were calculated for particles having radii: 250 nm, 400 nm and 500 nm. The extinction cross-section is defined as the ratio of the energy of light scattered and absorbed by the particle to the incident energy per unit area [9]. The equivalent spheres were subject to light-induced shrinkage in the same proportion as the grana, i.e. 13.6% in volume. The differences (light minus dark) between the cross-sections as functions of wavelength are plotted in Fig. 6.4. The positions of the maxima depend on the sizes and vary from around 510 nm for the smallest particle to 518 nm for the largest. The curves show also minima around 490 nm.

The above explanation of the 520 nm difference band should be treated as a qualitative one. Nevertheless, since we are able to demonstrate this by the application of selective dispersion to a granum model which includes a light-induced shrinkage effect it would seem that the intuitive model is an approach to reality. For simplicity we have assumed that light-induced shrinkage involves only the compression of the intervening cytoplasmic layers, however in practice the lipid membrane also appears to undergo a light-induced reduction in thickness. This latter change serves only however to enhance the nature of the selective dispersion demonstrated, with the maximum optical effects still occurring in the region of 520 nm.

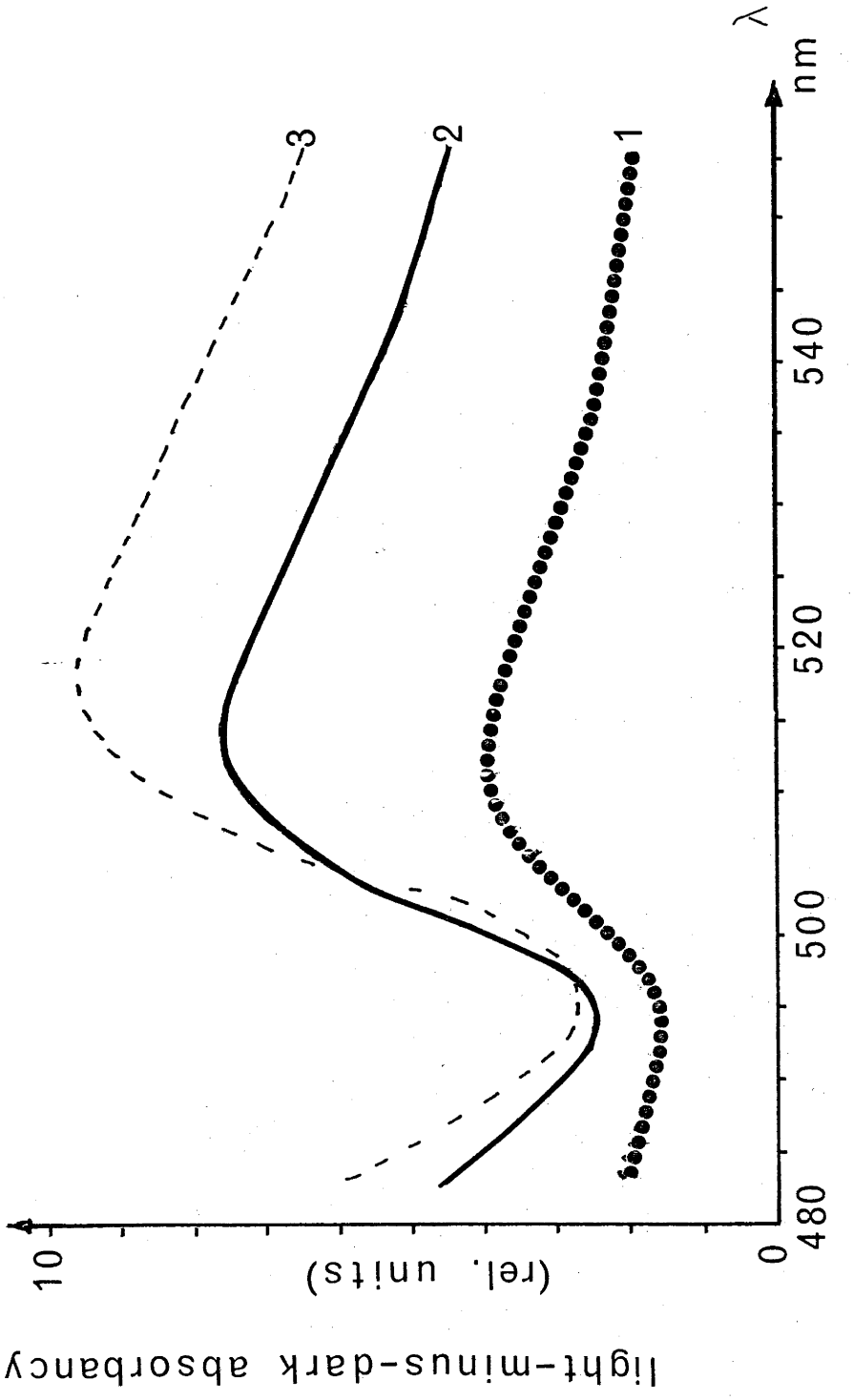

Fig. 6.4. The light minus dark extinction cross-sections of spherical particles consisting of grana thylakoids. In dark the radii of the particles are: 250 nm (curve 1), 400 nm (curve 2) and 500 nm (curve 3).

We conclude then that the light-induced shrinkage of the grana structures is indeed responsible for both the slow light-induced absorbancy and 90^{o} light scattering changes which peak in the region of 520 nm. This peak region is determined by the selective dispersion effect associated with the absorbancy bands of the carotenoids and chlorophylls.

6.3 Mathematical details

Several characteristics of light absorbing materials can be described in terms of the linear damped harmonic oscillator model of the dielectric permittivities [9]. If the material has N absorption frequencies ω_ℓ, $\ell = 1, 2, \ldots, N$, then its dielectric permittivity can be expressed by an equation

$$\varepsilon(\omega) = 1 + \sum_{\ell=1}^{N} \frac{C_\ell}{1-(\omega/\omega_\ell)^2 - i\gamma_\ell\omega/\omega_\ell^2} \tag{6.1}$$

where the frequency ω is related to the wavelength λ through the relation $\omega = 2\pi c/\lambda$, λ_ℓ are "damping factors" related to the half widths of the absorption peaks, and C_ℓ are the absorption strength constants of these. The coefficients C_ℓ can be calculated when the dielectric permittivity is known for frequencies between the absorption bands [11]. In the present case we consider two pigments: chlorophyll and β-carotene. Denote the dielectric permittivities of pure materials by ε_{chl} for Chl a and ε_{car} for the other. According to eq (6.1) we can write:

$$\varepsilon_{chl} = 1 + \frac{C_1}{1-\omega^2/\omega_1^2 - i\gamma_1\omega/\omega_1^2} + \frac{C_2}{1-\omega^2/\omega_2^2 - i\gamma_2\omega/\omega_2^2} + C_3, \tag{6.2}$$

$$\varepsilon_{car} = 1 + \frac{C_4}{1-\omega^2/\omega_3^2 - i\gamma_3\omega/\omega_3^2} + C_5 . \tag{6.3}$$

Here, ω_1 and ω_2, correspond to the absorption wavelengths of Chl a: 676 nm and 438 nm, respectively, whilst ω_3 corresponds to the wavelength of 500 nm taken as the peak absorption for β-carotene in vivo [1]. For the sake of simplicity we considered only one peak of β-carotene; that, which is related to the 520 nm difference band. The constants C_3 and C_5 account for contributions from the ultraviolet parts of the spectra; unforunately these are not well known, so we make the assumption that these parts of the absorption spectra contribute as much as the visible ones to the dielectric permittivities. For frequencies in the microwave region, when $\omega << \omega_1, \omega_2, \omega_3$, the values of ε_{chl} and ε_{car} should not differ much from the dielectric permittivities of other lipids which may be taken as 2.2. Hence from eqs (6.2) and (6.3) we obtain in the low frequency limit:

$$1 + C_1 + C_2 + C_3 = 1 + C_4 + C_5 \simeq 2.2 \quad . \tag{6.4}$$

For simplicity we assume that the extinction coefficients of the 676 nm and 438 nm absorption peaks are of the same order, and so $C_1 = C_2$; then, having in mind the ultraviolet contributions to the permittivities, we obtain

$$\text{a)}\ C_1 = C_2 = 0.2, \quad \text{b)}\ C_3 = 0.6, \quad \text{c)}\ C_4 = C_5 = 0.6 \quad . \tag{6.5}$$

The constants γ_1, γ_2 and γ_3 are estimated from the halfwidths of the absorption peaks; in the calculations the values used are: $\gamma_1 = \gamma_2 = 0.14 \times 10^{15} s^{-1}$, $\gamma_3 = 0.12 \times 10^{15}\ s^{-1}$.

In the protein-chlorophyll complexes and in the lipid bilayer surrounding them the pigments form only fractions of the total mass. We use the following simple interpolation formulae to express the dielectric

constants of the protein-chlorophyll spheres, ε_s, and their lipid-carotene surround, ε_m:

$$\varepsilon_s = 1 + v_p(\varepsilon_p - 1) + (1 - v_p)(\varepsilon_{chl} - 1) , \tag{6.6}$$

$$\varepsilon_m = 1 + v_\ell(\varepsilon_\ell - 1) + (1 - v_\ell)(\varepsilon_{car} - 1) , \tag{6.7}$$

where ε_p and ε_c are the permittivities of nonabsorbing in the visible region protein and lipid, respectively. In the calculations we use the values: $v_p = 0.65$ and $v_\ell = 0.95$, which are simply the corresponding mass fractions of proteins in the spheres and nonabsorbing lipids in the bilayer [8].

The dielectric constant of each cytoplasm layer between membranes changes as the thickness of each layer decreases, since some water is expelled with an increase in the proportion of suspended protein particles. To account for these changes we use the Lorentz-Lorenz formula [9], which relates the dielectric permittivity of a medium to the polarizability of its molecules. For protein particles suspended in aqueous sucrose of permittivity ε_w, the composite dielectric constant ε_c can be found from the equation:

$$\frac{\varepsilon_c - \varepsilon_w}{\varepsilon_c + 2\varepsilon_w} = f\frac{\varepsilon_p - \varepsilon_w}{\varepsilon_p + 2\varepsilon_w} \tag{6.8}$$

where f is the volume fraction of the protein particles in the cytoplasmic layer. It is difficult to estimate this volume fraction, so we fit such value of it which yields $\varepsilon_c = (1.35)^2 = 1.82$ in the dark adapted state, given $\varepsilon_w = 1.77$ and $\varepsilon_p = 2.4$ [12]. When grana are illuminated by light, shrinkage occurs and the volume fraction, f, and ε_c both rise. A decrease of thickness by 50%, as we assume in the model calculations, brings about the doubling of the volume fraction and the increase in ε_c

to 1.90 (refractive index $n_c = 1.38$).

Finally, we proceed to calculate the dielectric permittivity of whole grana. We apply formulae derived in relation to a birefringence problem in vision research by Ninham and Sammut [12]. From these formulae we can calculate the dielectric constant of the structure shown in Fig. 6.1; given the permittivities of the components: ε_s for the spheres, ε_m for their lipid surround and ε_c for the composite cytoplasm layers. Firstly, the dielectric properties of a plane of spheres of radius a, centre-to-centre separation b, are equivalent to those of an anisotropic dielectric slab of the thickness 2a and the permittivities:

$$\varepsilon_{pl}^{\perp} = \varepsilon_m \left(\frac{\Delta_{ms} - 9.0338(a/b)^3}{\Delta_{ms} - 9.0338(a/b)^3 + 2\pi a^2/b^2} \right) \tag{6.9}$$

$$\varepsilon_{pl}^{\parallel} = \varepsilon_m \left(\frac{\Delta_{ms} + 4.5169(a/b)^3 - 2\pi a^2/b^2}{\Delta_{ms} + 4.5169(a/b)^3} \right) \tag{6.10}$$

in the directions perpendicular and parallel to the plane, respectively. The quantity Δ_{ms} is defined by

$$\Delta_{ms} = \frac{2\varepsilon_m + \varepsilon_s}{\varepsilon_m - \varepsilon_s} \quad . \tag{6.11}$$

Secondly, the medium consisting of stacks of these slabs, separated by intervening cytoplasmic layers of dielectric permittivity ε_c and thickness l_c (see Fig. 6.1) has the permittivities [9,12]:

$$\varepsilon^{\perp} = (l_c + 2a)(l_c/\varepsilon_c + 2a/\varepsilon_{pl}^{\perp}) \quad , \tag{6.12}$$

$$\varepsilon^{\parallel} = (l_c\varepsilon_c + 2a\varepsilon_{pl}^{\parallel})/(l_c + 2a) \quad . \tag{6.13}$$

Note that eqs (6.12, 6.13) are valid even when the thickness of the layers

vary, provided that the overall structure is periodic and that the spatial period is small compared with the wavelength of light. In such a case, l_c should be replaced by the mean over the period.

Now, the refractive indices of grana for light polarized parallel to the membranes, $m^{\parallel}$, and for light polarized perpendicularly to them, $m^{\perp}$, are readily obtained from eqs (6.12, 6.13) by applying the familiar Maxwell relations:

$$\text{a)} \quad (m^{\parallel})^2 = \varepsilon^{\parallel} , \qquad \text{b)} \quad (m^{\perp})^2 = \varepsilon^{\perp} . \tag{6.14}$$

Eqs (6.14a,b) conclude the calculation of the refractive indices of grana. Both $m^{\parallel}$ and $m^{\perp}$ are complex since such are the permittivities ε_m and ε_s. The light-induced changes in grana structures are reflected in changes of values of $m^{\parallel}$ and $m^{\perp}$ since a) the thickness l_c is decreased (compare eqs (6.12, 6.13)) and b) the value of ε_c is changed with the increase in the fraction of protein particles suspended in the cytoplasm (eq (6.8)).

In order to calculate the light-induced absorbancy changes we identify a granum structure of chloroplasts with an equivalent spherical particle of radius R and the mean refractive index $m' = (2m^{\parallel} + m^{\perp})/3$. The particle is assumed to be in a medium of the refractive index $n_0 = 1.34$. Denote by m the relative refractive index of the particle: $m = m'/n_0$. Denote also the real part of m by n and the imaginary part by $-k$, so that $m = n - ik$. We apply van de Hulst equation of anomalous diffraction [5,13] to calculate the extinction efficiency of the particle - Q_{ext} :

$$\begin{aligned} Q_{ext} = {} & 2 - 4\exp(-\rho\tan\beta)(\cos\beta/\rho)\sin(\rho-\beta) \\ & - 4\exp(-\rho\tan\beta)[(\cos\beta)^2/\rho^2]\cos(\rho-2\beta) \\ & + 4(\cos\beta/\rho)^2\cos 2\beta , \end{aligned} \tag{6.15}$$

where $\rho = 4\pi R(n-1)/\lambda$ and $\tan\beta = k/(n-1)$. The extinction efficiency is defined as the energy of light scattered and absorbed by the particle to the incident energy geometrically intercepted by the particle; the extinction cross-section, C_{ext}, is related to Q_{ext} by the formula:

$$C_{ext} = \pi R^2 Q_{ext} \quad . \tag{6.16}$$

Eq. (6.15) applies only to particles larger than the wavelength of light. There are, however, empirical corrections derived by Deirmendijan [14,13], which bring the values of Q_{ext} to within ±4% of the exact ones calculated from Mie's theory. The corrected value of the extinction efficiency is:

$$Q'_{ext} = (1 + D_i)Q_{ext} \quad , \tag{6.17}$$

where Q_{ext} is given by (6.15) and the factors D_i are specified for four ranges of ρ provided that $1 < n \leq 1.50$ and $0 \leq k \leq 0.25$:

$$D_1 = 0.61(n-1)^2[F(\beta)+1]/n-[5(n-1)-\rho]/[5(n-1)F(\beta)] \quad , \tag{6.18}$$

for $\rho \leq 5(n-1) < 4.08/(1+3\tan\beta)$,

$$D_2 = 0.123(n-1)[F(\beta)+1]\rho/n \quad , \tag{6.19}$$

for $5(n-1) \leq \rho \leq 4.08/(1+3\tan\beta)$,

$$D_3 = 0.5(n-1)[F(\beta)+1]/[n(1+3\tan\beta)] \quad , \tag{6.20}$$

for $4.08/(1+3\tan\beta) \leq \rho \leq 4.08/(1+\tan\beta)$,

$$D_4 = 2.04(n-1)[F(\beta)+1]/[n\rho F(\beta)] \quad , \tag{6.21}$$

for $\rho > 4.08/(1+\tan\beta)$. In the above equations $F(\beta)$ is defined by

$$F(\beta) = (1+\tan\beta)(1+3\tan\beta). \tag{6.22}$$

The calculations which serve to plot Fig. 6.4 are performed for three particles having radii: 250 nm, 400 nm and 500 nm. Upon illumination they are taken to shrink to 216 nm, 345.6 nm and 432 nm, respectively. Their refractive index, m, changes in the way described above. The absorbancy changes are proportional to the changes in the extinction cross-sections, since the absorbancy, E, is related to C_{ext} by the equation (Latimer *et al* [4]):

$$E = 0.434\ L\ N\ C_{ext}\ , \tag{6.23}$$

where $E = \log_{10}(1/\text{transmission})$, L is the vessel thickness and N is the concentration of particles.

To conclude this section it seems worthwhile to discuss to what degree the measured scattering and absorbancy changes are due to the grana formations. Apart from the grana, light is also scattered and absorbed at stroma membranes and chloroplast envelopes. However, as the measurements of Krause show [15], for chloroplast suspensions in which grana are artificially unstacked the absorbancy and scattering are significantly lower compared with intact chloroplasts. Thus the absorbancy and scattering changes must be due predominantly to the changes within the grana. This also supports the view that the development of grana is necessary to achieve increased absorbancy of light by chloroplasts.

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